Low-Temperature Homoepitaxial Growth with SiCl₄ Precursor Compared to HCl Assisted SiH₄-based Growth

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Abstract. Chlorinated silicon precursor SiCl₄ was investigated as a source of additional chlorine instead of or in combination with HCl during the low-temperature (1300°C) halo-carbon epitaxial growth. No Si cluster cloud was visible inside the hot-wall susceptor indicating negligible homogeneous gas-phase nucleation. The growth rate was significantly enhanced compared to the SiH₄-case, but was relatively close to the SiH₄+HCl case. Similar to the SiH₄+HCl growth, the increase of the growth rate caused by suppressed cluster formation was less significant than expected. The depletion of the growth species by vigorous polycrystalline deposition upstream of the hot zone, which was earlier reported for the SiH₄+HCl growth, was also significant in the SiCl₄-based growth. Closer to the growth zone, carbon species also get incorporated in the polycrystalline deposits.

Introduction

In our previous work, low-temperature halo-carbon epitaxial growth (at 1300°C) was conducted with SiH₄ silicon precursor and HCl addition in order to reduce undesirable effects of the homogeneous gas-phase nucleation leading to formation of silicon clusters in the gas phase [1,2]. It was established that premature dissociation (or suppressed formation) of Si gas-phase clusters in the upstream portion of the hot zone of the reactor may cause undesirable effects. Such dissociation enhances the polycrystalline deposition on the walls of the hot zone, thus leading to significant precursor depletion, which reduces the benefits of the HCl addition.

Other chloride-based CVD technique has been developed, where chlorine is added to the gas mixture by use of some chlorinated silicon precursors instead of using HCl[3-5].

In this work, chlorinated silicon precursor SiCl₄ was investigated and compared to SiH₄+HCl as a source of additional chlorine to suppress the homogeneous nucleation, while avoiding premature release of silicon from the silicon precursor.

Experiment

Pieces of commercial 4H-SiC wafers vicinally cut 8⁰ towards the [11-20] direction were used as substrates for epitaxial growth. The growth of 4H-SiC films was conducted in a low-pressure hot-wall CVD reactor at 1300°C and 150 Torr with H₂ as the carrier gas and CH₃Cl as the carbon source. Silane (SiH₄) or silicon tetrachloride (SiCl₄) was used as the silicon precursor. HCl was added during the growth as an additional source of chlorine, with flow rates from 0 to 25 sccm.

The epilayer thickness maps were obtained by reflective Fourier Transform Infrared Spectroscopy (FTIR). Surface morphology was examined by Nomarski optical microscopy. Capacitance-voltage (C-V) measurements were used to characterize unintentional doping. Rigacu Ultima III X-ray diffractometer was used to analyze the relative contents of different phases in the polycrystalline deposits that were formed at different regions of the hot zone of the reactor.
Results and Discussion

Precursor depletion in SiH\textsubscript{4}+HCl growth.

The silicon cluster cloud was visibly reduced (though not completely eliminated) when HCl was added during the growth with SiH\textsubscript{4} precursor, thus indicating that significant suppression of the homogeneous nucleation in the gas phase took place.

As was first reported in the previous work [2], HCl causes a complex influence on low-temperature growth (Fig. 1). The HCl dependence of the growth rate and doping cannot be explained by a simple model suggesting that HCl-enhanced dissociation of silicon clusters in the gas phase merely leads to additional supply of silicon species for the epitaxial growth. While \( R_g \) does significantly increase at least for some HCl flow rates, there are regions of HCl dependence where the trend temporarily reverses (e.g., HCl flow rate of 8 sccm compared to 5 sccm in Fig. 1).

Complex changes in the effective silicon-to-carbon ratio caused by HCl were observed when monitoring the changes in doping (Fig. 1). It was concluded that the supply of carbon species may also be enhanced at least at low HCl flows. This fact supported a hypothesis that the gas-phase clusters may contain a significant amount of carbon in addition to silicon (i.e., Si-Si\textsubscript{x}C\textsubscript{y} clusters) as was previously suggested by other groups [6,7].

It was observed that polycrystalline deposition takes place in the upstream portion of the hot zone. The pattern of the polycrystalline deposition was monitored by placing small pieces of 4H-SiC substrates at different locations in the hot zone along the gas flow direction upstream from the growth zone similar to the approach used in Ref.2. The leftmost micrographs in Fig. 2 (i.e., micrographs (a1), (a2), and (a3)) correspond to the most upstream samples. Each micrograph in Fig. 2 has a corresponding number in millimeters, indicating the distance from the leading edge of the susceptor (positive numbers for the samples placed on the susceptor and negative numbers for the samples placed on the thermal insulation foam upstream from the susceptor).

When SiH\textsubscript{4} is used as the silicon precursor without adding HCl, the homogeneous gas-phase nucleation competes with the island nucleation process, thus reducing the precursor consumption by the polycrystalline islands (Fig. 2(1)). When HCl is added, the polycrystalline deposition and the corresponding depletion of the growth species becomes much more significant (Fig. 2(2)), which is at least in part responsible for the non-monotonous dependence of \( R_g \) on the HCl flow rate (Fig. 1).

More detailed discussion of the carbon involvement in the gas phase clusters, precursor depletion by polycrystalline deposition during the low-temperature growth with SiH\textsubscript{4} precursor, and their role in the complex dependence of Fig. 1 is presented in Ref.2.

Precursor depletion in SiCl\textsubscript{4} growth. Absolutely no Si cluster cloud was observed inside the hot-wall susceptor when SiCl\textsubscript{4} precursor was used even at high precursor flow rates. \( R_g \) was significantly enhanced compared to the SiH\textsubscript{4}-case, but relatively close to the value of \( R_g \) in the SiH\textsubscript{4}+HCl case.

In Fig. 2, the pattern of polycrystalline deposition for the SiH\textsubscript{4} growth without and with HCl is compared to that during SiCl\textsubscript{4} growth.

The distance along the gas-flow direction where polycrystalline deposition first appeared was approximately the same for SiH\textsubscript{4} and SiH\textsubscript{4}+HCl cases (Fig. 2 (b1) and (b2)), corresponding to the...
onset of thermal decomposition of SiH$_4$. As was expected, slower decomposition of SiCl$_4$ resulted in absolutely no polycrystalline deposition (or epitaxial growth) at this upstream location (Fig. 2(b3)).

At more downstream locations of the hot zone, the polycrystalline deposition in SiCl$_4$ experiments became more similar to the SiH$_4$+HCl case, while different from the SiH$_4$ growth without HCl. As was reported earlier for SiH$_4$-without-HCl process [2], polycrystalline islands quickly disappeared when approaching the hot susceptor (Fig. 2(c1)). This was explained by formation of low-diffusivity gas-phase clusters making Si unavailable for polycrystalline deposition. Suppressed formation of Si clusters by the addition of HCl as well as when using SiCl$_4$ resulted in significant polycrystalline deposition in regions (c2) and (c3) of Fig. 2. The polycrystalline deposition depletes a portion of Si growth species released from the clusters, thus limiting the $R_g$ in the growth zone.

More careful comparison showed that the polycrystalline deposition in the SiCl$_4$ case is...
somewhat less significant, but lasts further downstream than in the SiH$_4$+HCl case, and can be observed closer to the growth zone (Fig. 2(f3)). This is apparently due to slower SiCl$_4$ dissociation and slower release of Si growth species compared to SiH$_4$.

**Composition of polycrystalline islands.** With help of Energy Dispersive Spectroscopy and X-ray diffraction, it was established that in all three cases considered, the polycrystalline deposits in the more upstream portion of the hot zone included only polycrystalline Si (Fig. 3a).

Further downstream, dissociation of the carbon precursor CH$_3$Cl led to incorporation of carbon in the polycrystalline deposits in the form of SiC (Fig. 3b). Consequently, use of both SiH$_4$+HCl and SiCl$_4$ process causes significant (and non-equal) depletion of silicon and carbon sources, even though this depletion may be less in SiCl$_4$ growth.

**Precursor flow dependencies.** HCl addition was also investigated for SiCl$_4$ growth. HCl caused small increase of $R_g$ of the order of 5-10%. This indicates that the homogeneous nucleation is not completely eliminated when SiCl$_4$ is used, and HCl can cause additional dissociation of the gas-phase clusters and reduction of precursor consumption by the clusters. There is no clear indication that HCl addition increases the degree of precursor depletion by the polycrystalline deposition mechanism, which was happening in the SiH$_4$+HCl growth.

The dependence of $R_g$ on SiCl$_4$ flow rate showed expected increase. This was different from the SiH$_4$+HCl case of weak dependence of $R_g$ on SiH$_4$ flow, supporting the conclusion that the silicon source depletion by polycrystalline deposition is less severe for SiCl$_4$ precursor. However, it should be noted that slower dissociation of SiCl$_4$ may lead to extension of the region of the polycrystalline deposition inside the growth zone when the same carrier gas flow rates are used.

**Summary**

Experiments with SiCl$_4$ precursor in place of SiH$_4$ during the low-temperature halo-carbon epitaxial growth clearly indicated drastically suppressed homogeneous nucleation in the gas phase due to the delayed dissociation of SiCl$_4$ precursor. The polycrystalline deposition in the upstream portion of the hot zone still takes place, although the region of this deposition is shifted more downstream (closer to the growth zone) when compared to SiH$_4$ growth. It appears that reduction of the precursor depletion by the polycrystalline deposition mechanism should be one of the important targets for further increase of the growth rate.

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**References**

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