Nitrogen Doping in Low-temperature Halo-carbon Homoepitaxial Growth of SiC

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Abstract. In this work, nitrogen doping was investigated during the low-temperature halo-carbon epitaxial growth of 4H-SiC on Si- and C-faces. The dependencies of nitrogen incorporation on nitrogen flow rate, Si/C ratio, growth rate, and temperature were investigated. It was established that the efficiency of nitrogen incorporation for the C-face growth at 1300 °C is higher than that for the Si-face for a wide range of the growth conditions. Seeming deviation of the Si/C ratio dependence from the “site-competition” trend confirmed the critical role of the silicon vapor condensation during the low-temperature epitaxy. Opposite trends for the nitrogen doping dependence on the growth rate were observed on the Si- and C-faces. Finally, a complex temperature dependence of the nitrogen doping in the temperature range from 1300 to 1450 °C was observed.

Introduction

In our previous work, use of a halo-carbon precursor enabled low-temperature homoepitaxial growth of 4H-SiC epitaxial layers at temperatures below 1300 °C with good quality [1]. A possibility of low-temperature selective epitaxial growth conducted with SiO\textsubscript{2} mask was demonstrated [2]. Very efficient n+ doping for C-face and p+ doping for Si-face epitaxial layers was achieved [3].

Prior to this work, nitrogen and aluminum incorporation during 4H- and 6H-SiC homoepitaxy was investigated only at temperatures above 1450-1500 °C (i.e., at regular growth temperatures) [4-6]. Utilization of low-temperature epitaxial growth for device applications requires knowledge of the main process dependencies for dopant incorporation.

Experimental

The halo-carbon epitaxial growth was conducted in a low-pressure hot-wall CVD reactor at 100-150 torr. Epilayers were grown on Si- and C-faces of commercial 4H-SiC wafers. H\textsubscript{2} was used as the carrier gas. Silane (SiH\textsubscript{4}) and chloromethane (CH\textsubscript{3}Cl) served as the silicon and the carbon sources respectively. The intentional nitrogen doping was performed during the growth by utilizing non-diluted nitrogen gas. Capacitance-voltage and SIMS techniques were used to characterize efficiency of nitrogen and aluminum incorporation and activation.

Results and Discussion

One of the pronounced characteristics of nitrogen and aluminum incorporation during the halo-carbon epitaxial growth at low temperatures is a strong dependence on the substrate orientation. In a wide range of growth conditions, more than an order of magnitude higher nitrogen concentration was achieved on C-face than on Si-face. An opposite dependence was earlier observed for aluminum doping, showing stronger aluminum incorporation on Si-face than on C-face [3].
Doping Dependence on N\textsubscript{2} flow. In the entire range of the N\textsubscript{2} flow rates attempted in this work, the nitrogen doping showed linear dependence on the nitrogen flow rates (Fig. 1). The slope of the linear dependences was the same for the Si- and C-face growth and close to unity. The previously obtained data points for the higher doped epitaxial layers measured by SIMS [3] (not shown in Fig. 1) approximately correspond to the extension of the same linear trends in the higher-doping region (beyond 10\textsuperscript{19} cm\textsuperscript{-3} for Si-face and beyond 10\textsuperscript{20} cm\textsuperscript{-3} for C-face) without any detectable change of the slope of the linear dependence.

Doping Dependence on Si/C Ratio. The dependence of the nitrogen incorporation on silicon-to-carbon ratio (Si/C) was investigated in order to establish if the site-competition mechanism is also dominating at low growth temperatures during the halo-carbon growth. The Si/C ratio was varied by increasing the SiH\textsubscript{4} flow and decreasing the CH\textsubscript{3}Cl flow to keep the growth rate constant. During the growth at 1300\textdegree C on Si-face, the nitrogen doping trend was consistent with the site-competition mechanism at relatively low Si/C ratios (i.e., showed the linear increase of the nitrogen incorporation with increasing the Si/C ratio) (Fig. 2). When the input Si/C ratio was increased above six (for the fixed growth rate of 1.5 µm/hr), further increase of the Si/C ratio caused progressively slower increase in nitrogen doping and eventually saturation of the doping concentration at high values of the Si/C ratio (Fig. 2).

This result is one of important confirmations for the previously suggested dominating influence of the silicon vapor condensation in the gas phase [1], which depletes the Si-related growth species and saturates the supply of Si species to the growth surface when the SiH\textsubscript{4} flow is increased beyond a certain point. Similar to the growth rate saturation with increasing the SiH\textsubscript{4} flow [1], nitrogen doping stops increasing at high values of the “input” Si/C ratio because the increase of the effective (or real) Si/C ratio above the growth surface saturates as a result of the Si vapor condensation.

Quantitatively different dependence of nitrogen incorporation on the Si/C ratio was observed when the growth was conducted on C-face of the 4H-SiC substrate (Fig. 2). In the entire range of the
Si/C ratios attempted in this work, much weaker dependence of nitrogen incorporation was observed on C-face. However, a certain weak trend of the nitrogen-doping growth with increasing the Si/C ratio is present at low values of Si/C ratio, followed by its saturation at higher Si/C ratios (Fig. 2), which is qualitatively similar to the Si-face dependence described above.

A similar trend of a weak dependence of the nitrogen incorporation on the Si/C ratio was previously reported for the epitaxial growth conducted at 1600°C [4]. It is possible that during the low-temperature growth (similar to the higher-temperature growth of Ref. 4) the predominant termination of the C-face with carbon atoms even at high Si supply makes the number of carbon vacancies virtually independent of the Si/C ratio. However, the explanation for this model that is based on a possibility of easy re-evaporation of the loosely bound Si atoms from the C-face surface suggested in Ref. 4 is less convenient due to the significantly lower temperatures used in our work.

Doping Dependence on the Growth Rate. In investigating the growth rate dependence, special precautions were taken to ensure not only a constant input Si/C ratio but also a constant effective Si/C ratio above the growth surface. For this purpose, the growth rate was conducted at relatively low SiH$_4$ flow rates to avoid Si vapor condensation that could result in unintentional decrease of the effective Si/C ratio. The growth rate was increased by increasing both SiH$_4$ and CH$_3$Cl flow rates.

The dependence of the nitrogen incorporation on the growth rate showed opposite trends for the Si- and C-faces (Fig. 3). Nitrogen incorporation on Si-face showed steep increase with increasing the growth rate. For the same growth conditions, the dependence was weak on C-face and showed moderate decrease of the nitrogen doping with increasing the growth rate.

Doping Dependence on the Growth Temperature. The temperature dependence was investigated in the temperature range from 1280°C (below which the surface morphology starts degrading quickly for the given growth conditions) and up to 1550°C. Similar to the growth rate dependence, the growth was conducted at low SiH$_4$ flow rates in order to minimize the deviation of the effective Si/C ratio from the input Si/C ratio caused by the Si vapor condensation. Both the SiH$_4$ and CH$_3$Cl flow rates were proportionally adjusted for each temperature to keep the growth rate constant while changing the growth temperature.

A complex dependence of the nitrogen doping on the growth temperature was established in the temperature range from 1280 to 1550°C (Fig. 4). The dependence is weak for the C-face. The temperature dependence was much stronger for the Si-face, and two regions of opposite and very strong temperature dependences were observed (Fig. 4).

It appears that more than one mechanism influences the temperature dependence in this relatively wide temperature range. It is not straightforward to decouple and identify the role of the mechanisms.
related to nitrogen transport and/or surface reactions in this experiment. It appears that the dominant influence of the temperature change may be coming from the unintentional change of the effective Si/C ratio with temperature due to different kinetics of silicon vapor condensation and Si cluster dissociation at different temperatures. It is suggested that with increasing the growth temperature, the effective Si/C ratio decreases thus leading to reduction in the efficiency of the nitrogen incorporation on Si-face as observed in Fig. 4. This explanation is supported by the fact that fairly unexpected degradation of the epilayer morphology took place when the temperature was increased from 1300 to beyond 1340°C. This kind of morphology degradation was also observed when we decreased the input Si/C ratio while keeping the other growth conditions constant.

When the growth temperature is further increased beyond 1450°C, the epilayer morphology improves and the nitrogen doping shows the trend of quick growth with increasing the temperature. We attribute this region of the temperature dependence to the increase of the effective Si/C ratio with temperature, possibly due to more efficient dissociation of Si clusters.

As was shown earlier, the nitrogen doping weakly depends on variations of the Si/C ratio on C-face. This supports our model of the Si/C ratio-related mechanism of the temperatures dependence and could explain why the temperature dependence on the C-face is weak (Fig. 4).

Summary

The trends of the doping dependences investigated in this work confirmed the strong influence of the Si vapor condensation limiting the supply of the Si species to the growth surface [1]. The study highlighted the importance and complexity of controlling the effective Si/C ratio when changing the growth rate, input Si/C ratio, and the temperature during the halo-carbon epitaxial growth. The exact origin of the complex dependence of doping on the growth temperature (which was attributed in this work to drastic change of the effective Si/C ratio when the temperature is increased) remains unclear. The observed trend is expected to shine additional light on the kinetics of the gas phase reactions of silane and chloromethane decomposition in the low-temperature range of homoepitaxial growth.

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References