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Incorporation of dopants in epitaxial SiC layers grown with fluorinated CVD chemistry

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Fluorinated chemistry in chemical vapor deposition (CVD) of silicon carbide (SiC) with SiF₄ as Si precursor has been shown to fully eliminate formation of silicon clusters in the gas phase making SiF₄ an interesting Si precursor. However, before a fluorinated CVD chemistry can be adopted, the effect of fluorine on the dopant incorporation must be understood since dopant incorporation is of paramount importance in semiconductor manufacturing. Here, we present dopant incorporation studies for n-type doping with N using N₂ and p-type doping with Al using TMAI in fluorinated CVD of homoepitaxial SiC. The precursors used were SiF₄ as Si precursor and the source of F together with CH₄ as C precursor. We find that it is possible to control the doping in SiC epitaxial layers when using a fluorinated CVD chemistry for both n- and p-type material using the C/Si ratio as in standard SiC CVD. However, large area doping uniformity seems to be a challenge for a fluorinated CVD chemistry, most likely due to the very strong Si-F and Al-F bonds.

I. INTRODUCTION

Silicon carbide (SiC) is a wide band-gap semiconductor with outstanding potential for high-temperature, high-power and high frequency applications.^{1,2} The hot wall, horizontal chemical vapor deposition (CVD) method is the most studied and best suited technique for growing the epitaxial layers which serve as the active region in all electronic SiC devices.³ The demands on the layers differ substantially between different applications, e.g. power devices require thick (30 – 100 μm), low-doped ($10^{13} - 10^{15}\text{cm}^{-3}$) layers whereas high-frequency devices require thinner (in the μm range) layers with moderate doping (10^{17}cm^{-3}). The standard approach to SiC CVD is to use silane, SiH_4 , and small hydrocarbons e.g. propane, C_3H_8 , or ethylene, C_2H_4 , as precursors diluted in a hydrogen carrier gas flow. The typical growth temperature is 1550 – 1650 $^\circ\text{C}$ rendering growth rates in the range 5 – 20 $\mu\text{m/h}$ range.⁴ In order to increase the growth rate, mainly for production of high power devices, several routes to high growth rate SiC CVD has been explored. As SiC CVD is done in the mass transport controlled CVD regime, in order to increase the growth rate, the amount of Si and C growth species impinging the substrate surface must be increased. This is typically achieved by increasing the flow of the precursors into the CVD reactor. The main problem with a higher precursor flow is homogeneous gas phase nucleation, mainly formation of silicon droplets. This can be avoided by doing CVD at a lower total pressure which will in turn yield a lower partial pressure of Si, lowering the probability for Si droplet formation.⁵ Another route is to add a chemical species that outcompetes the formation of Si-Si bonds by forming bonds to Si stronger than the Si-Si bond. For this route, addition of chlorine has been studied in great detail,⁶ but it has also been shown that addition of bromine⁷ or fluorine⁸ have the same effect.

Of paramount importance when depositing electronic device structures is the ability to control the amount of incorporated dopants in the material. Aluminum and nitrogen are the most common dopants in SiC for p-type respectively n-type doped layers. In SiC CVD these are typically introduced as trimethyl aluminum (TMAI) and dinitrogen (N_2). The substitutional incorporation of Al and N in the SiC lattice is controlled by the site-competition theory where Al is thought to replace Si and N is thought to replace C in the SiC lattice.⁹ This makes the C/Si ratio in the CVD gas mixture the key parameter for controlling the amount of incorporated dopants. Doping incorporation in a chlorinated chemistry has been studied in detail and it was found that n-type doping by N_2 and tertbutylphosphine (TBP: $C_4H_9PH_2$) for doping with phosphorus was easily done and not affected by the presence of chlorine,¹⁰ while p-type doping by TMAI and triethylboron (TEB: $B(C_2H_5)_3$) were both affected by the presence of chlorine which limited the maximum net carrier concentration to the low 10^{18} cm^{-3} range for Al doping and to the low 10^{19} cm^{-3} range for B doping.¹¹ This was suggested to be due to formation of volatile monochlorides, AlCl and BCl at the CVD conditions, 1570 °C and 200 mbar. This is also supported by thermochemical modeling.¹² This hypothesis is further supported by a p-type doping study in low temperature CVD of SiC with chlorinated chemistry at 1300 °C, where the stability of AlCl is lower,¹² where Al doping in the 10^{20} cm^{-3} range was measured by SIMS.¹³ Two overall conclusions from the doping studies with a chlorinated chemistry are that the C/Si ratio can still be used to control the doping and that chlorine seems to decrease the incorporation of p-type dopants. No detailed doping study has been done with a brominated chemistry, but it was reported that the net carrier concentration in the unintentionally doped layers were n-type,

where the n-type conductivity stemmed from the background doping in the CVD reactor, decreased with a higher C/Si ratio in the CVD gas mixture into the reactor.⁷ This behavior is expected from the site competition theory. No doping studies have been reported for a fluorinated chemistry in SiC CVD. In this paper we present a study on how n-type doping by N₂ and p-type doping by TMAI is affected by the presence of fluorine in the CVD process when using SiF₄ as Si precursor for SiC CVD.

II. EXPERIMENTAL

For the growth of epitaxial SiC layers, a horizontal hot wall CVD reactor without rotation was used. The growth chamber was a SiC coated graphite susceptor with a gas cross section of 78 mm × 24 mm in width and height, respectively, and a length of 190 mm, which was preceded by a SiC coated widened graphite inlet after gas liner made of quartz. Substrates pieces of 4H-SiC and a 4° off-cut angle, 16 mm × 16 mm in size, were placed at 3, 6 and 9 cm into the susceptor from the susceptor inlet. As precursors SiF₄, CH₄ and N₂ or TMAI were used as Si, C and N or Al precursors, respectively. SiF₄ also acted as the source of F. The precursors were diluted in Palladium membrane purified H₂ acting as the carrier gas. For the experiments a carrier gas flow of 37.5 standard liters per minute (SLM) at a process pressure of 100 mbar was used. This gives a room temperature corresponding average gas speed velocity of 3.3 m/s in the susceptor. The process temperature was 1600 °C and the Si/H₂ = 0.125 %.

When investigating doping using N₂, the C/Si ratio was first fixed at 1.0 and the N₂/Si ratio was varied from 0.1 to 10, then the N₂/Si was fixed at 1.0 and the C/Si ratio was varied from 0.4 to 1.2 in steps of 0.2. Experiments where the N₂/Si was reduced

proportional to the C/Si ratio to keep $N_2/C = 1$ as the C/Si was varied from 0.4 to 1.0 were also done. One additional experiment using 5 SLM of N_2 was made to supplement the series of increased N_2 flow for a N_2/Si ratio of 100. To retain the average gas velocity and keeping the process pressure, the amount of carrier gas was reduced from 37.5 SLM to 32.5 SLM, otherwise keeping the flow rates of SiF_4 and CH_4 , thereby resulting in a Si/ H_2 ratio of 0.144 % instead of 0.125 %. When investigating doping using TMAI the C/Si ratio was kept at 1.0 while varying the Al/Si ratio in the range from 10^{-5} to 10^{-2} and varying in the C/Si ratio in the interval 0.4 to 1.2 in steps of 0.2 when $Al/Si = 10^{-4}$.

For measurement of the net donor and acceptor concentration, capacitance-voltage measurements were used using a mercury probe station. The thickness of the grown epitaxial layers was approximated from the extension of triangular defects¹⁴ on the sample at least 2 mm away from the sample edge to avoid growth rate edge effects. The extension of the triangular defects was measured using optical microscope.

III. RESULTS

The samples were grown with a growth rate of 8.0-10.3 $\mu m/h$ (depending on the C/Si ratio) measured on the sample positioned 3 cm from the inlet shown in Fig 1. On the average, the growth rate increased slowly as the C/Si ratio is increased.

FIG. 1. Growth rate with varied C/Si ratio measured on the sample positioned 3 cm from the inlet.

A. *n*-type doping using N_2

In the examined range of N_2 /Si ratio, the net donor concentration varies approximately linearly with the amount of dopant (Fig 2). By comparing the net donor concentration in the samples positioned at 3, 6 and 9 cm from the inlet, it is here also observed that the net donor concentration is higher further downstream in the susceptor. By lowering the C/Si ratio from 1.2 down to 0.4 (Fig 3), the net carrier concentration increases approximately $\frac{3}{4}$ of a magnitude, i.e. almost 6 times higher incorporation, although the growth rate is reduced by 30 %. The incorporation is slightly enhanced even if the flow of N_2 is reduced proportionally to the C/Si ratio (Fig 4). Even though the growth rate drops 30 % the net donor concentration increases 30 % - 50 %.

FIG. 2. Net donor concentrations when varying the N_2/Si ratio. Since $C/Si = 1$, this implies that $N_2/Si = N_2/C$. A trend of increasing net donor concentration can be seen as the N_2/Si ratio is increased. Here, the result from the experiment using a reduced flow of H_2 to compensate of the increased flow of N_2 is plotted at $N_2/Si = 100$ ($Si/H_2 = 0.144\%$, 32.5 SLM H_2 instead of $Si/H_2 = 0.125\%$, 37.5 SLM H_2).

FIG. 3. Net donor concentrations when varying the C/Si ratio. On the average, the net donor concentration is observed to change oppositely to the C/Si ratio, i.e. a decreased net donor concentration can be observed for an increased C/Si ratio.

FIG. 4. Net donor concentrations when N_2/Si and C/Si reduced equally. A slightly oppositely change in net donor concentration to the C/Si ratio, i.e. decreasing net donor concentration incorporation can be observed for an increased C/Si ratio.

B. *p-type doping using TMAI*

When TMAI is used for p-type doping the net acceptor concentration is approximately linear to the Al/Si ratio in the interval of experiments (Fig 5). For the dependence on the C/Si ratio, an increase of approximately 60 % is observed as the C/Si is increased from 0.4 to 1.2 (Fig 6). In this case, the net acceptor concentration should be put in the perspective of a 30 % increased growth rate in the same interval, as was shown in Fig 1. The net acceptor concentration for the 3 cm samples are significantly higher than the net acceptor concentrations for the 6 and 9 cm samples. For p-type doping using

TMAI, the net acceptor concentration decreases along the susceptor, which is the opposite for the case for the incorporation of N.

FIG. 5. Net acceptor concentrations when varying the Al/Si ratio. A trend of increased net donor concentrations can be observed for increased Al/Si ratios.

FIG. 6. Net acceptor concentrations when varying the C/Si ratio. An increased net acceptor concentration can be observed for an increased C/Si ratio. Note the significantly higher net acceptor concentration at 3 cm from the inlet.

IV. DISCUSSION

It is possible to see a slightly increasing growth rate as the C/Si ratio is increased. The increase is though not proportional to the C/Si ratio, indicating that the growth is in the Si limited regime. The slight increase of the growth rate is due to that the growth starts further downstream in the susceptor as the C/Si ratio is increased. From the starting position of the growth, the growth rate decreases slowly along the susceptor, giving rise to a slightly higher growth rate at certain positions as the C/Si ratio is increased.¹⁵ It was ascribed to a changing effective C/Si ratio that decreased along the susceptor, i.e. higher effective C/Si ratio upstream and lower effective C/Si downstream. The drop in growth rate is most likely due to higher F content downstream, terminating the Si surface layer.¹⁶

As the net donor and acceptor concentrations followed the increment of N₂ and TMAI, respectively, we assume that the net donor and acceptor concentration is from the incorporation of N and Al, respectively, and thereby that the net donor and acceptor concentration is the N and Al concentration in the SiC lattice.

A. *n-type doping using N₂*

Incorporation of N is controlled by the C/Si ratio as seen for the n-type doping using N₂ when varying the C/Si ratio (Fig. 3). Although the growth rate change of 30 % in the C/Si ratio range of 0.4 to 1.2 can affect the incorporation, the change of growth rate is fairly insignificant compared to the 6 times higher N incorporation in the same interval. It is also possible to observe an increase in the N incorporation further downstream along

the susceptor. That goes well in hand with the suggestion that the effective C/Si ratio decreases along the susceptor. There can also be a chemical reason for this; that N containing dopant species are formed slowly. For the chlorinated chemistry it has been suggested by Cavallotti et al. that SiN is an important N dopant species.¹⁷ In the fluorinated chemistry the Si species is not formed in high concentrations.¹⁵ Together with the stable N₂ molecule another reason for the increasing dopant incorporation along the gas flow can be that the kinetics of forming N dopant species is slow, thereby forming more such species downstream, creating a higher dopant concentration downstream. Albeit a low concentration of Si species and a high effective C/Si ratio, the dopant incorporation was still limited by the supply of N₂, which could be seen by the linear relationship of dopant incorporation and the N₂/Si ratio in Fig 2. Still in the 10¹⁷ range of N concentration, the inclusion of N is linear with the N₂/Si concentration. The C/Si ratio is therefore suggested to mainly be controlling the surface adsorption of the N dopant species, where a lower C/Si ratio allows for a higher surface adsorption which is in line with the site competition theory⁹. The incorporation of N depending on the C/Si seen in Fig 3 is approximately exponentially decaying (linear on the logarithmic scale used in the graph) in the studied C/Si ratio interval while the N incorporation is approximately linear versus the N₂/Si ratio seen in Fig 2. In Fig 4, where the N₂/C ratio is kept constant and the C/Si ratio is varied we see an increment in the incorporation, which we attribute to that the exponential behavior is dominant over the linear N₂/Si behavior.

We have when using N₂ for n-type doping in the fluoride chemistry identified two ways of controlling the dopant incorporation – changing the C/Si ratio or changing the N₂/Si ratio. If the process requires a special C/Si, there is a possibility to alter the N₂/Si

ratio to reach the targeted dopant concentration. The doping homogeneity over large areas is though poor, most likely due to varying effective C/Si ratio in the gas phase, affecting the surface.

B. p-type doping using TMAI

For the p-type doping with Al using TMAI, probably the most prominent difference compared to the n-type doping using N₂ is that the Al incorporation is not as strongly dependent on the C/Si ratio and that the doping concentration was showed to increase with the C/Si ratio. Even taking into account that the growth rate could influence the incorporation, the result is in line with the site competition theory⁹. For the incorporation of Al, higher doping levels are observed upstream where the effective C/Si ratio is expected to be higher than downstream where the opposite conditions prevail. This could also be said to be in line with the site competition theory if the amount of Al dopant species are mainly the same along the susceptor. The Al dopant species was suggested by Cavallotti et al. to be the Al atom.¹⁷ As HF is present in the fluorinated chemistry, and the Al-F bond is stronger than the H-F bond with bond dissociation energies 675 kJ/mol and 570 kJ/mol¹⁸, respectively, it is possible that F forms a bond with Al in a similar manner as in the chlorinated chemistry where AlCl is expected to form,¹² thereby reducing the amount of Al dopant species further downstream in the susceptor. If it would only have been the change in effective C/Si ratio (i.e. surface reactions) that influenced the Al incorporation there would not have been a significant higher dopant incorporation upstream (Fig 6) for the full range of C/Si ratios as the effective C/Si changes along the susceptor. This indicate that another mechanism prevail

as well, which we suggest is the reduced amount of atomic Al in the gas phase due to the formation of AlF species.

The drop in net acceptor concentration for lower concentrations of TMAI is most likely due to the n-type background in the reactor, but could also arise from reduced amount of atomic Al species at low Al/Si ratios due to higher fraction of AlF species at low Al concentrations.

V. SUMMARY AND CONCLUSIONS

It is possible to control the doping in SiC epitaxial layers when using a fluorinated CVD chemistry for n- and p-type material using the dopants N₂ and TMAI, respectively. The dopant incorporation can be controlled by the amount of supplied dopants and by the C/Si ratio, according to the site competition theory. The large area doping uniformity seems to be a challenge for a fluorinated CVD chemistry, likely due to the expected slow kinetics of the SiF₄ precursor caused by the very strong Si-F bonds. We further believe that the gas phase chemistry plays an important role for the amount of created dopant species to be incorporated into the SiC lattice by reducing the amount of available Al through AlF formation.

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