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The 4H-SiC Epitaxy Study of Ammonia Doping

Yuebin Han[1,a], Zheyang Li[2,3,b*], Yingxi Niu[4,c], Da Li[1,d], Honglei Yan[1,e], Jianxin Shi[1,f]

[1]SiCentury Semiconductor Technology (Suzhou) Co., Ltd, Jiangsu Province, 215021, China

[2]Beijing Huairou Laboratory, Beijing, 101499, China

[3]Beijing Institute of Smart Energy, Beijing, 102209, China

[4]Institute of Semiconductors, Chinese Academy of Sciences, Beijing, 100083, China

[a]hanshan@sicentury.com, [b]lizheyang@bise.hrl.ac.cn, [c]yingxiniu@163.com, [d]dali@sicentury.com, [e]kevinyan@sicentury.com, [f]kellyshi@sicentury.com

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Abstract. Silicon carbide (SiC) is one of the ideal electronic materials for producing high-temperature, high-frequency, and high-power electronic devices. In the past 20 years, with the continuous improvement of silicon carbide material processing technology, its application has been expanding. Unlike Si devices, SiC devices cannot be directly fabricated on crude wafers. Instead, epitaxial films need to be deposited and grown on SiC wafers, then the epitaxial films will be used to as the foundation for producing devices. The doping concentration performance of the epitaxial layer can determine the device performance, making it the most important indicator of the epitaxial layer quality. For a long time, nitrogen has been used as the dopant in the production of SiC epi-wafers. Due to the difficulty of nitrogen cracking and its adsorption in graphite, the concentration is prone to significant drift, resulting in a decrease in yield and low production efficiency. In this research a unique vertical epitaxial process was used to consecutively grow 10 8-inch SiC substrates with nitrogen and ammonia as dopant separately. The concentration and thickness of the grown epitaxial films was measured and studied. The results indicate that compared to nitrogen as a dopant, the results of ammonia doping are significantly better in terms of intra-wafer concentration uniformity and inter-wafer consistency. Using nitrogen as the dopant, the doping concentrations uniformity of epi-layer ranges from 1.31% to 2.18%, and the deviation is between ± 8.0%. As a comparison, using ammonia as the dopant, the doping concentration uniformity of epi-layer ranges from 0.65% to 0.89%, and the deviation is between ± 1.0%. Meanwhile, the thickness performance is maintained at the same level. Therefore, ammonia as a dopant can solve the concentration drift problem that has long been a headache in large-scale production of SiC epitaxy, greatly improving production efficiency. Its advantages are obvious. This study analyzed the most significant reasons for the superior performance of ammonia gas as a dopant for 4H SiC epitaxy compared to nitrogen.

Introduction

SiC, as a typical representative of third-generation wide bandgap semiconductor materials, has the characteristics of high critical breakdown field strength, high thermal conductivity, high electron saturation drift velocity, large bandgap width, and strong radiation resistance [1,2]. It can meet the requirements of the next generation of power electronic equipment for working under harsh conditions such as higher power, smaller size, and high temperature and radiation [3,4,5]. It has the advantages of reducing size, decreasing power loss, and lower cooling requirements. SiC has become an essential material for high-end applications in power electronics, bringing revolutionary changes in fields such as new energy vehicles, photovoltaics, energy storage, rail transit, and smart grids [6,7]. In the past few years, the popularity of electric vehicles has driven a continuous supply shortage of SiC power devices [8,9].

Different from the typical Si semiconductor manufacturing process, SiC devices must be processed on the epitaxial film. Therefore, silicon carbide epitaxial equipment plays a critical connecting role in the whole industrial chain, and it is also the most complex and difficult to develop equipment in the whole industrial chain. The doping concentration performance of the epitaxial layer can determine device performance and is the most important indicator for measuring the quality of epi-wafers in epitaxial mass production. At present, SiC power devices are mainly produced from 6-inch wafers. The shipping standards for mainstream epitaxial manufacturers' 6-inch epitaxial wafers are: thickness uniformity ≤ 3%, doping concentration uniformity ≤ 5%, and defect density (triangle + downfall) $\leq 0.5cm^{-2}$. In the past 20 years, with the continuous improvement of epitaxial equipment and processes, the growth rate and quality of silicon carbide epitaxial films have been greatly improved, which has correspondingly promoted their widespread application in more fields. With the development of 8-inch wafer technology, the current shipping standards for 8-inch epitaxial wafers are basically on par with 6-inch wafers.

Nitrogen has long been used as dopant for N-type doping in SiC research and industry due to its availability, low cost, and inherent safety. At the same time, the industry has had to withstand its significant drawback, which is, the tendency to drift and poor stability of doping concentration. When conducting batch epi-growth, the doping concentration will change from one epi-wafer to another, especially for equipment utilizing a horizontal process flow, which has a large range of variation and can easily exceed the set shipping standards. In order to avoid the epi-wafer scrap, resulting from doping concentration out of spec, epi-wafer manufacturers have had to test every epi-wafer and determine the adjustment plan for the next epi-wafer prior to proceeding the next epi-growth. Alternatively, based on the test results, adjustments can be made up to every 3 wafers, which leads to a significant decrease in production efficiency. Against the backdrop of the surging demand for SiC power chips, together with the tightening of shipping standards, the concentration drift of nitrogen doping has become an urgent issue that needs to be addressed. Analyzing the reasons, a speculation is that due to the high chemical stability of nitrogen, it is very difficult to crack, resulting in a very low proportion of active nitrogen atoms which can be doped. A large amount of nitrogen is adsorbed and accumulated in the cavity by graphite components. During the heating process of the next epi-growth, the newly introduced nitrogen and the accumulated and released nitrogen will gradually lift up the doping concentration. Contrarily, when ammonia was used as dopant, the doping process will be carried out in a more controlled way. In this research a vertical epitaxial equipment was used to consecutively grow 10 8-inch SiC epi-wafers using nitrogen and ammonia as dopant separately. The concentration and thickness of the grown epi-layers were detected and studied, and the prospects of ammonia replacing nitrogen as dopant were investigated.

Experiment

The homogeneous epitaxial growth experiment in this study was conducted in the SiC epitaxial CVD equipment developed by SiCentury Company. Here the process utilizes a vertical type, hot-wall, 6/8-inch compatible, equipped with high-speed rotation technology. Previous studies[10,11] and production practices have demonstrated the very good performance of this equipment using nitrogen as dopant on 6-inch and 8-inch SiC epitaxy. Figure 1 shows the schematic structure of its process chamber, which consists of a spray head, a hot wall, a tray rotating device, a side resistance heating system, and a bottom resistance heating system. The process gas is vertically injected into the chamber through the top spray head, and reaches the substrate surface through a hood to undergo epitaxial growth reaction. The substrate is heated by the bottom heaters and rotated by a high-speed rotating system. The SiC substrate is a double-side polished 4H SiC substrate, purchased from Tankeblue Company. SiC thin film was grown on a 4H SiC wafer with a diameter of 200mm on the Si surface. The reaction gases were TCS and C_2H_4, with flow rates of 850 and 140 mL/min, respectively. H_2 and HCl gases were used for pre-etching and surface preparation. The H_2 carrier gas, purified by an Ag-Pd purifier, flow rate is 120slm and the reaction chamber pressure is 250 mbar. The temperature for epitaxial growth is 1650 ℃. Table 1 summarizes the process growth conditions of this study.

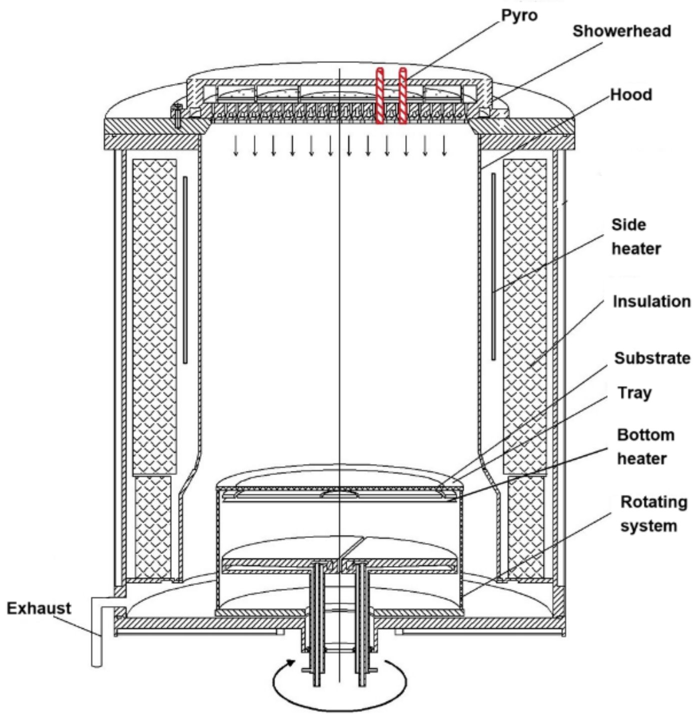

Fig. 1. Schematic drawing of high-speed rotation vertical hot-wall CVD process chamber.

Table 1. Table of epitaxial parameters.

Epi-growth Parameters	Set value	Unit
Temperature	1650	[°C]
Pressure	200~400	[mbar]
Rotation Speed	400~600	[r/min]
C/Si	0.8~1.2	—
Si/H_2	2.8%	—
Cl/Si	3.2	—

The thickness of the epitaxial film was measured using a ThermoFisher Nicolet IS50 Fourier transform infrared spectrometer (FTIR), the doping concentration was measured using a 4D CVMAP 92A mercury probe C-V tester, and the edge exclusion was 5.0mm.

Results and Discussion

Epitaxial Growth Results by Using Nitrogen as Dopant. Firstly, nitrogen was used as dopant to carry out 10 consecutive homogeneous epi-growth on 8-inch SiC wafers. During the growth period, the recipe was slightly adjusted based on the tested doping concentration results, especially in run # 5/6/7 where the nitrogen flow rate was reduced to ensure that the doping concentration met the shipping standards. The test results of 10 epi-wafers are as follows: the average doping concentration is $9.59 \times 10^{15}cm^{-3}$, the uniformity of doping concentration ranges from 1.31% to 2.18%, with the average uniformity of 1.84%, the deviation of the average concentration to the target value is between ± 8.0%, and the average absolute deviation is 3.57%; The average thickness is 11.14μm, and the thickness uniformity ranges from 1.0% to 2.0%, with the average uniformity of 1.38%. The deviation of the average thickness to the target value is between ± 2.0%, and the average absolute deviation is

0.37%. Figures 2-5 show the intra-wafer uniformity and deviation of 10 consecutive samples with doping concentration and thickness, respectively. Compared with the shipping standards for epi-wafers mentioned in the introduction, it can be found that the uniformity of the experimental results has reached the standard of 6-inch epitaxial wafers, meeting the requirements for mass shipment. However, it can be found from Figure 3 that the fluctuation of doping concentration is relatively big, and in large-scale production, even slight production management deviation can easily lead to out of spec and scrap, subsequently affecting production efficiency.

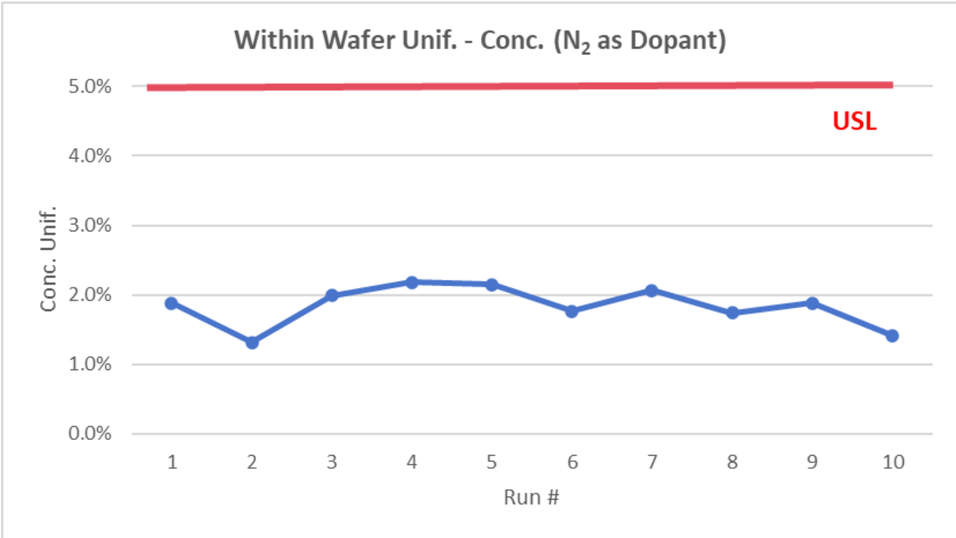

Fig. 2. Doping Concentration Uniformity of 10 Consecutive Runs (N_2 as Dopant).

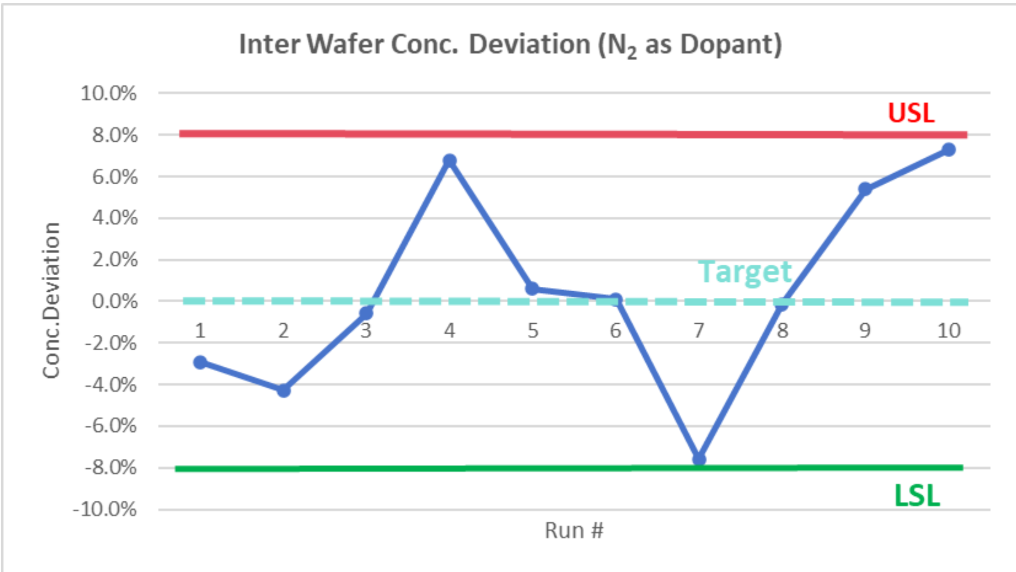

Fig. 3. Doping Concentration Average Deviation of 10 Consecutive Runs (N_2 as Dopant).

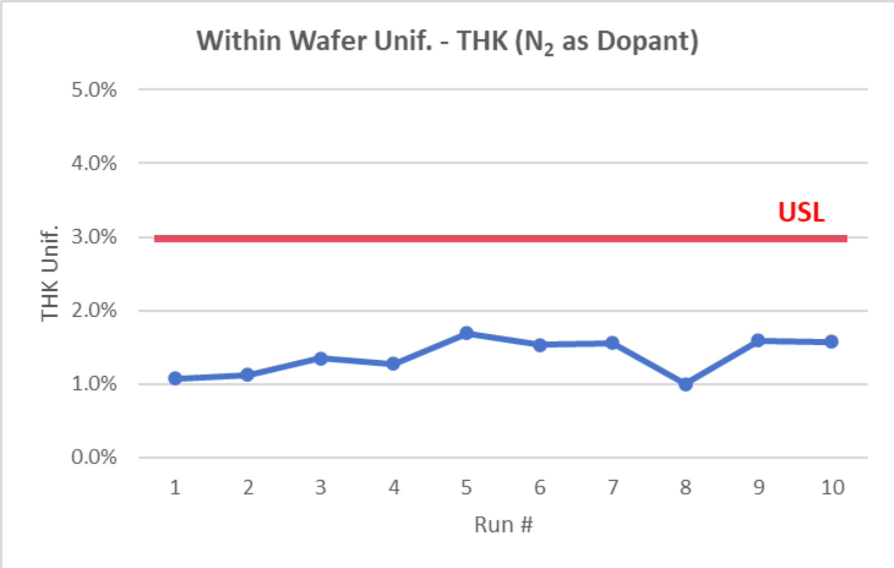

Fig. 4. Thickness Uniformity of 10 Consecutive Runs (N_2 as Dopant).

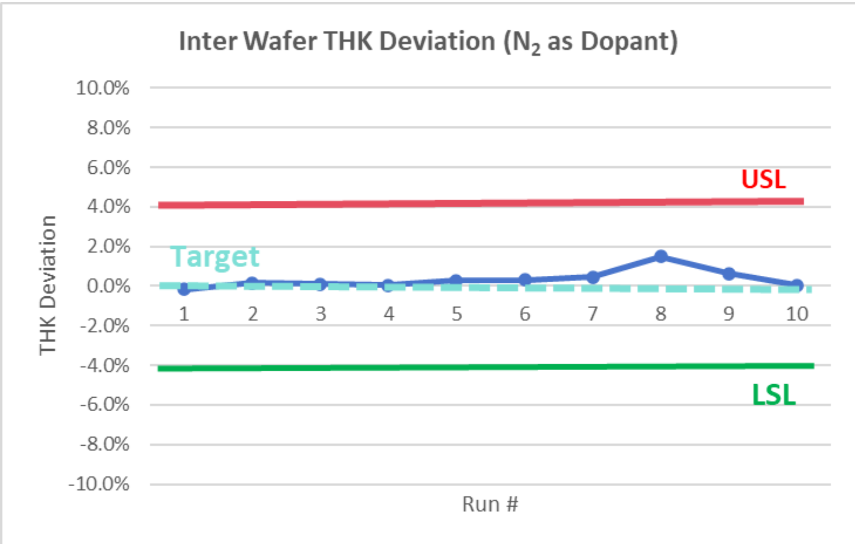

Fig. 5. Thickness Average Deviation of 10 Consecutive Runs (N_2 as Dopant).

Epitaxial Growth Results by Using Ammonia as Dopant. Then, ammonia was used as dopant to carry out 10 consecutive homogeneous epi-growth on 8-inch SiC wafers, keeping the recipe completely unchanged. The test results of 10 epi-wafers are as follows: the average doping concentration is $7.48 \times 10^{15}cm^{-3}$, the uniformity of doping concentration ranges from 0.5% to 1.0%, with the average uniformity of 0.76%, the deviation of the average concentration to the target value is between ± 1.0%, and the average absolute deviation is 0.42%; The average thickness is 11.14μm, and the thickness uniformity ranges from 1.0% to 2.0%, with the average uniformity of 1.25%. The deviation of the average thickness to the target value is between ± 2.0%, and the average absolute deviation is 0.77%. Figures 6-9 show the intra-wafer uniformity and deviation of 10 consecutive samples with doping concentration and thickness, respectively. Compared with the shipping standards for epi-wafers mentioned in the introduction, it can be found that the uniformity has reached the level of 6-inch excellent epi-wafers, fully meeting the requirements for mass shipment. Data shows that there is basically no change in the performance of thickness, surface roughness, and surface defects of the epitaxial film in the two situations of nitrogen and ammonia as dopant, and the biggest difference is about doping concentration performance. The average uniformity of doping concentration is 0.76% by using ammonia, which is significantly reduced from 1.84% by using nitrogen as dopant, and the deviation is between ± 1.0% by using ammonia, which is significantly decreased from ± 8.0% by using nitrogen as the dopant. Therefore, it can be concluded that using ammonia as dopant significantly increase the uniformity and reduce the deviation of doping concentration, which can solve the long-lasting concentration drift problem in SiC industry, greatly improve production efficiency, and is very beneficial to SiC mass production.

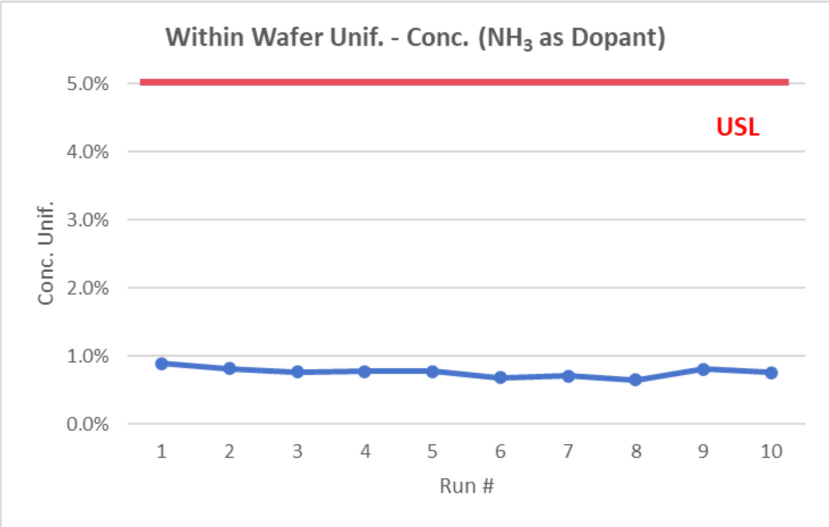

Fig. 6. Doping Concentration Uniformity of 10 Consecutive Runs (NH_3 as Dopant).

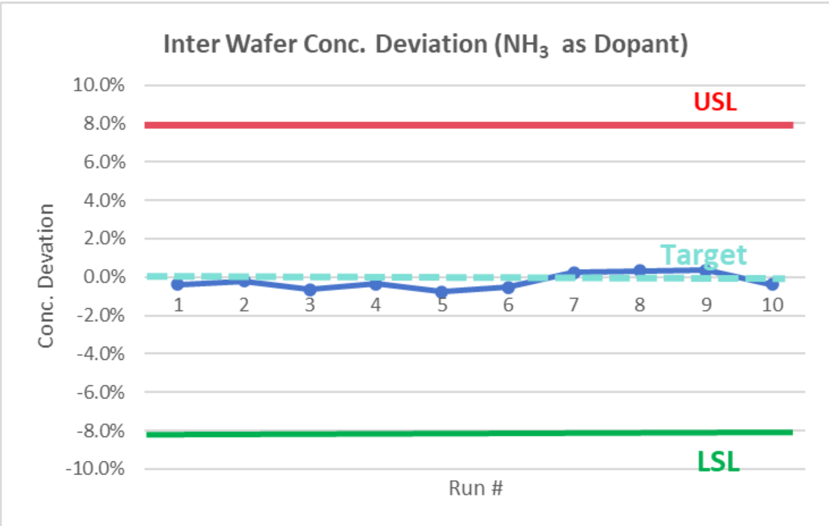

Fig. 7. Doping Concentration Average Deviation of 10 Consecutive Runs (NH_3 as Dopant).

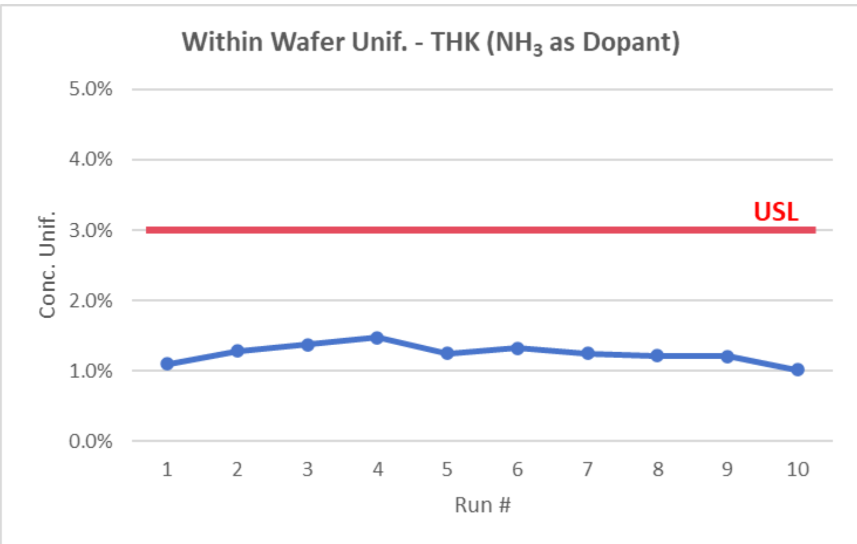

Fig. 8. Thickness Uniformity of 10 Consecutive Runs (NH_3 as Dopant).

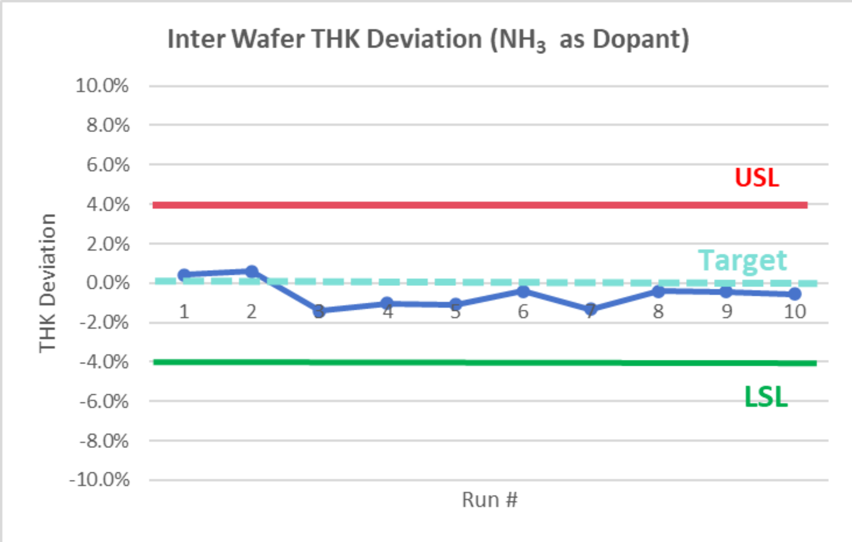

Fig. 9. Thickness Average Deviation of 10 Consecutive Runs (NH_3 as Dopant).

To investigate the impact of dopant to defect density, SICA88 was employed to measure the 10 epi-wafers by nitrogen and 10 epi-wafers by ammonia separately. The results show the average killer defect (carrot, triangle and downfall) density in both cases are 0.027 cm^{-2} and 0.025 cm^{-2} respectively, indicating that the dopants have almost no impact to defect density.

Analysis of Experimental Results. From the experimental results, it can be concluded that compared with using nitrogen as dopant, using ammonia as dopant, by comparing Figure 6 and Figure 2, it can be observed that the uniformity of the within-wafer doping concentration is significantly reduced from an average of 1.84% to 0.76%; by comparing Figure 7 and Figure 3, it can be observed that the deviation of doping concentration has significantly decreased from an average of 3.57% to 0.42%. The significant improvements in these two aspects can be analyzed from the chemical characteristics and adsorption properties of ammonia gas.

Nitrogen molecules are bound by N-N triple bonds, which are very strong and difficult to break. The bond energy is as high as 942KJ/mol, so its cracking is very difficult. For instance, its decomposition temperature under atmospheric pressure is about 3000 °C. This determines that at a SiC epi-growth temperature of around 1600°C, the proportion of nitrogen that can be decomposed into active nitrogen atoms is very low. The N-H bond energy in ammonia molecules is only 389kJ/mol, so its cracking is relatively much easier, with decomposition temperature of around 400 °C. This means that at the epi-growth temperature of SiC around 1600°C, the proportion of active nitrogen atoms is significantly increased when using ammonia vs. nitrogen as dopant. Because the graphite component inside the reaction chamber is a porous material with strong adsorption capacity. A large amount of nitrogen is adsorbed and accumulated in the cavity by graphite components. During the heating process of the next run, because of the addition of the newly introduced nitrogen and the accumulated released nitrogen, the doping concentration will gradually increase, which is often difficult to predict. As shown in Figure 3, in prior to adjusting the nitrogen flow rate, the concentration deviation gradually increases from Run #2 to Run #4, and from Run #7 to Run #10, which is the result of accumulation. Graphite is prone to adsorb more nitrogen than ammonia [12]. Therefore, when using ammonia as dopant, the doping process in each epi-growth mainly depends on the active nitrogen atoms cracked during the epi-growth, without cumulative effects, in which good inter-wafer uniformity and inter-wafer consistency cand be relatively easily achieved compared with nitrogen. This is reflected that the concentration deviation of each run shown in Figure 7 is very small, showing there is no cumulative effect.

When nitrogen is used as dopant in epi-growth, the main reason for the deterioration of inter-wafer uniformity is the increasing doping concentration at the edge while the concentration remains stable in the center area. The increasing doping concentration at the edge is because new loose particles are constantly generated at the edge of the tray during every epi-growth, which increases the adsorption of nitrogen and gradually increases the doping concentration at the edge area, while the center area remains flat and unchanged, resulting in the continuous increase of within-wafer uniformity. When ammonia is used as dopant, the adsorption at the edge points is weak, and the doping concentration at the edge area remains stable, resulting in a significant improvement in within-wafer uniformity.

The primary challenge in using ammonia doping process is to prevent blockages at both the inlet and exhaust ends. Special designs are required to achieve that at both ends. The design at the inlet end aims to prevent NH_3 and HCl from contact and reacting at low temperatures. The design at the exhaust end aims to directly introduce the unreacted excessive NH_3 into the exhaust treatment system, also avoiding contact HCl.

Conclusion

The research results indicate that compared to nitrogen as dopant, the use of ammonia as dopant results is significantly better for within-wafer concentration uniformity and inter-wafer consistency. When using nitrogen as dopant to consecutively carry out 10 epi-growth, an average within-wafer uniformity of 1.84% and mean concentration deviation of ± 8.0% can be achieved. In comparison, when using ammonia as dopant to consecutively carry out 10 epi-growth, an average within-wafer uniformity of 0.76% and mean concentration deviation of ± 1.0% can be achieved. Clearly, the conclusion can be drawn that using ammonia as dopant significantly increases the uniformity and reduces the deviation of doping concentration. These significant improvements will contribute to solving the long-lasting concentration drift problem in SiC epitaxial production, greatly improving production efficiency, and is very profitable to large-scale production. The advantages of ammonia as dopant are obvious. The next step of research should focus on studying and verifying the performance of epi-wafers doped with ammonia in the chip manufacturing process and final device, paving the way for the large-scale use of ammonia as dopant in SiC epitaxial production.

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References

[1] CASADY J, JOHNSON R., Status of silicon carbide (SiC) as a wide- bandgap semiconductor for high-temperature applications: a review, Solid State Electron, 39 (1996) 1409-1422.

[2] MORKOC H, STRITE S, GAO G, et al., Large-band-gap SiC, III-V nitride, and II-VI Zn Se-based semiconductor-device technologies, Journal of Applied Physics, 76 (1994) 1363-1398.

[3] EDDY J, GASKILL D., Silicon carbide as a platform for power electronics, Science, 324(2009) 1398-1400.

[4] LEE T, BHUNIA S, MEHREGANY M., Electromechanical computing at 500 ℃ with silicon carbide, Science, 329 (2010) 1316-1318.

[5] Yuebin Han, Yong Pu, Jianxin Shi, Advances in Chemical Vapor Deposition Equipment Used for SiC Epitaxy, J Synth Cryst., 51(2022):1300-1307.

[6] P.J. Wellmann, Review of SiC crystal growth technology, Semicond. Sci. Technol. 33 (2018) 103001.

[7] X. She, A.Q. Huang, O. Lucìa, B. Ozpineci, Review of silicon carbide power devices and their applications, IEEE Trans. Ind. Electron. 64 (2017) 8193–8205.

[8] Information on http://semiengineering.com/sic-demand-growing-faster-than-supply/.

[9] Information on http:// compoundsemiconductor.net/article/106023/Infineon_Tackles_SiC_Supply_Shortages%7BfeatureExtra%7D/.

[10] Yuebin Han, Yong Pu, Jianxin Shi & Honglei Yan. Epitaxial Growth Study of n-Type 4H-SiC Films by High-Speed Wafer Rotation Vertical Hot-Wall CVD Equipment, J Synth Cryst. 52(2023) 918-924.

[11] Jingrui Han, Xiguang Li, Yongmei Li, et al. Substrate Preparation and Epitaxy for the Production of 200-mm SiC wafers, J Synth Cryst. 53(2024) 1712-1719.

[12] Huitao Gu, (2012). The Study of Removal of Low-concentration Ammonia from Nitrogen by Adsorption. (Doctoral dissertation, Dalian University of Technology).