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Optimization of SiC Cleaning Process Based on Zeta Potential

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Abstract: This The SiC is a polar semiconductor that is easy to adsorb particles due to the surface charges, which results in that the RCA process commonly used for silicon cleaning is not good for SiC cleaning, and the technique should be optimized. To check the surface charge of SiC wafers during the cleaning process, this work investigated the adsorption of polystyrene spheres (PS) on SiC epitaxial wafers at different pH values and measured the Zeta potential of the SiC wafers. We analyzed the mechanisms by which the Zeta potential in alkaline (SC1) and acidic (SC2) cleaning solutions affects the adsorption of particles on SiC epitaxial wafers surface. The results showed that both the SiC epitaxial wafers and the particles had a negative Zeta potential in the SC1 cleaning solution and there was an electrostatic repulsion between them. In contrast, in the SC2 cleaning solution, the SiC epitaxial wafers and particles had opposite Zeta potentials, which caused attraction between the wafers and particles. Therefore, based on the analysis of Zeta potential, we proposed an optimized the SiC cleaning process that use SC2 cleaning before SC1 cleaning. We successfully reduced the number of particles attached to the surface of SiC epitaxial wafers by 80.4% than RCA cleaning process by the optimized cleaning process. The optimized cleaning process would have a practical value due to the reduction on the consumption of time and chemical reagents.

Keywords: Silicon Carbide, Zeta potential, Wafer cleaning, RCA process, Particle contamination.

1. Introduction

Silicon Carbide (SiC) is an exemplary wide bandgap semiconductor material that possesses excellent characteristics such as high breakdown voltage, high saturation electron drift velocity, high thermal conductivity, and high thermal stability[1]. It is an ideal material for manufacturing high-power electronic devices. As a polar semiconductor, SiC is prone to adsorption of contaminating particles due to its charged surface[2]. These particles may cause problems such as circuit interruption or short-circuiting in subsequent device manufacturing[3], which can further affect the manufacturing yield and stability of the devices[4]. Therefore, developing effective cleaning processes is crucial in SiC semiconductor manufacturing[5].

Domestic and foreign scholars have conducted extensive research on the cleaning process of SiC materials for a long time. Based on the cleaning environment, it can be divided into dry cleaning and wet cleaning. Among these, the research on dry cleaning processes mainly includes the following: Guan et al[6]. proposed a two-step method that involved H_2:He (1:1) plasma treatment and heating at a temperature below 1000°C to obtain a clean C-terminated SiC surface. Huang et al[7]. proposed an electron cyclotron resonance hydrogen plasma cleaning method, which can achieve an atomically flat and clean unreconstructed surface after 5 minutes of treatment at a low temperature (200-700°C). Losurdo et al[8]. found that a clean SiC surface can be obtained by treating SiC material with atomic hydrogen at 200°C.

Dry cleaning has strict environmental conditions and low production efficiency, which limits its widespread use in SiC material cleaning. In contrast, wet cleaning has lower temperature requirements and can be carried out under atmospheric pressure. Moreover, it can clean multiple wafers simultaneously, making it the mainstream technology for SiC cleaning in industrial production[9].

The wet cleaning process commonly used in the SiC industry originates from the standard RCA cleaning method for silicon (Si). The SPM (mixture of concentrated sulfuric acid and hydrogen peroxide) cleaning solution is primarily used to remove organic contaminants, while the SC1 (mixture of ammonia, hydrogen peroxide, and DI water) cleaning solution is mainly used to eliminate particle contamination and a small amount of metal ion contamination. The SC2 (mixture of hydrochloric acid, hydrogen peroxide, and DI water) cleaning solution is primarily used to remove metal ion contamination[10].

However, the RCA cleaning process of silicon carbide still faces various issues, including susceptibility to the influence of equipment and operators, excessive use of chemical agents, generation of excessive wastewater, and repetitive cleaning. To enhance the efficiency and stability of the silicon carbide cleaning process, it is particularly important to explore its cleaning mechanism. This paper first studied the Zeta potential of the commonly found contaminants on the surface of silicon carbide epitaxial wafers under different pH conditions. This was based on the results of an adsorption experiment of polystyrene balls on the silicon carbide epitaxial wafer. Then, a cleaning experiment was designed to investigate the effect of Zeta potential on particles in the SC1 and SC2 cleaning solutions. Finally, based on the research results of Zeta potential, the standard RCA cleaning process adopted by the silicon carbide industry was optimized. The verification experiments show that the improved cleaning process significantly enhances the removal effect of surface particles and reduces process costs.

2. Experimental

2.1. Materials

The SiC wafer cleaning process was validated using 4H-SiC epitaxial wafers. The wafer size was 4 inches, with an epitaxial layer thickness of 12 μm and a doping concentration of 5×10^{16} cm^{-3}. The material used for the PS sphere adsorption experiment was a surface aminated polystyrene (PS) microsphere solution with a particle size of 1 μm and solid content of 2.5%. The test samples for the PS sphere adsorption experiment were 10×10 mm^2 slices of the aforementioned epitaxial wafers. In accordance with the requirements of the Zeta potential tester, 36×15 mm^2 epitaxial wafer slices were used to measure the Zeta potential.

2.2. Methods

Sun, Tao et al[11]. proposed that the Zeta potential directly affects the surface charge of polystyrene microspheres and measured the Zeta potential of surface-aminated polystyrene microspheres as a function of pH. They found that the Zeta potential of polystyrene microspheres is positive in acidic solutions, while it is negative in alkaline solutions.

Two solutions were prepared using dilute hydrochloric acid and KOH solid to obtain pH values of 2 and 12, respectively. A 0.1 ml PS sphere solution was mixed with the water solutions of varying pH. 10×10mm^2 epitaxial wafers were then immersed in the solutions for 30 seconds, removed, and allowed to dry naturally. An optical microscope was used to observe the distribution of PS spheres on the SiC sample surface.

The 4-inch epitaxial wafer was placed in a single wafer carrier with an open box lid and left in a Class 1000 cleanroom for more than three days, during which a considerable amount of particles contaminated its surface. Subsequently, the wafer was subjected to group cleaning using a chemical cleaning tank, according to the conditions listed in Table 1, in a Class 10 cleanroom.

Table 1. Experimental wafers and corresponding cleaning processes

Sample No.	Cleaning process
A	SPM→SC1→SC2
B	SPM→SC1
C	SPM→SC2
D	SPM→SC2→SC1

Sample A served as the control experiment and was cleaned only using conventional RCA technology. Sample B was cleaned using SPM and SC1 processes to investigate the particle removal effect of the SC1 process. Sample C was cleaned using SPM and SC2 processes to investigate the particle removal effect of the SC2 process. Sample D had its cleaning process order adjusted, with SC2 being completed before SC1, to investigate the effect of the order of SC1 and SC2 processes on particle removal efficiency.

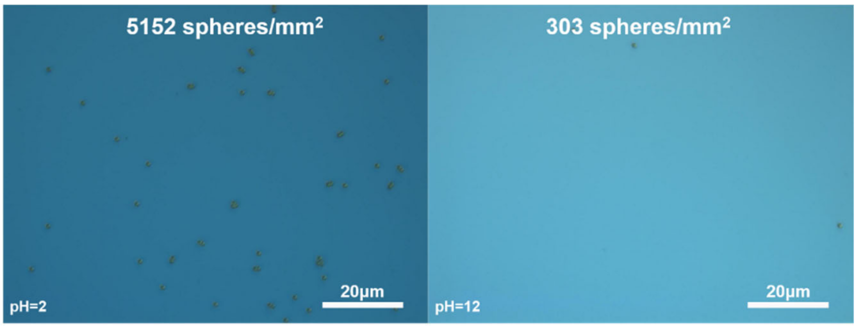
Following each step in the cleaning process, the samples were rinsed with ultrapure water and subjected to ultrasonic cleaning. After the cleaning process was complete, nitrogen gas was used to dry the samples, which were then placed in clean wafer carriers for further testing.

2.3. Techniques of analysis

In this study, the Leica DM8000M semiconductor polarizing microscope was used to detect the adsorption of PS spheres on the 10×10mm^2 epitaxial wafer. The Otsuka Electronics ELSZ-2000ZS potential analyzer was used to measure the Zeta potential of the Si surface of the epitaxial wafer. The surface defect detection equipment (Lasertech company SICA) was used to detect the number of residual contaminating particles on the Si surface of the epitaxial wafer (labeled as A-D).

3. Results and Discussion

SiC is a polar semiconductor that is primarily used in the industry for epitaxial growth and device manufacturing on Si surfaces[12]. As a result, this paper focuses on the charge state of the Si surface of SiC wafers. Figure 1 illustrates the adsorption of PS spheres on the Si surface of SiC epitaxial wafers in solutions with pH values of 2 and 12, respectively. In Figure 1(a), where the solution pH is 2, the Si surface of the epitaxial wafer adsorbs a large number of PS spheres, with a statistically calculated surface adsorption density of 5152 spheres/mm^2. However, in Figure 1(b), where the solution pH is 12, the Si surface only adsorbs a small amount of PS spheres, with a statistically calculated surface adsorption density of only 303 spheres/mm^2. The significant difference in the PS sphere adsorption density on the SiC surface in Figure 1 demonstrates that the solution pH value is the determining factor that affects the amount of PS sphere adsorption.



(a) (b)

Figure 1. The adhesion density of PS spheres at pH 2 (a) and pH 12 (b)

We hypothesize that the observed results can be attributed to the interaction between the Zeta potential of the Si surface of the epitaxial wafer and that of the PS spheres[13]. To confirm this hypothesis, we measured the Zeta potential of the Si surface of the epitaxial wafer in solutions of varying pH values and compared it with the Zeta potential of the PS spheres under the corresponding pH conditions. This investigation was carried out to better understand the mechanism behind their interaction.

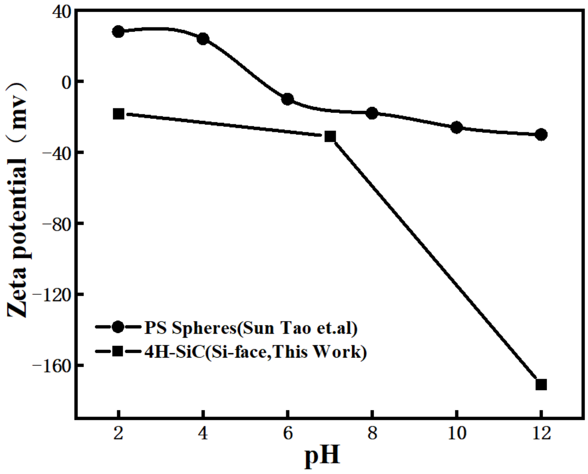


Figure 2. Zeta potential variation of PS spheres and Si-face of SiC epitaxial wafers with pH

Figure 2 illustrates the Zeta potential variation of the PS spheres and the Si surface of the epitaxial wafer as a function of pH. Both Zeta potentials gradually decrease with increasing pH. At pH 2, the Zeta potential of the PS spheres is positive, while that of the Si surface of the epitaxial wafer is negative, creating an electrical attraction between them. Consequently, a large number of PS spheres are adsorbed onto the Si surface of the epitaxial wafer. At pH 7 and 12, both the PS spheres and the Si surface of the epitaxial wafer exhibit negative Zeta potentials, resulting in electrical repulsion between them. Moreover, the absolute value of the Zeta potential of the Si surface of the epitaxial wafer significantly increases at pH 12, which strengthens the electrical repulsion. Consequently, only a small number of PS spheres are adsorbed on the epitaxial wafer surface. These findings suggest that the Zeta potential is a crucial factor in the mechanism of particle adsorption onto the epitaxial wafer.

In actual production processes, the particle pollutants on the SiC wafer surface mainly consist of SiO_2, Al2O3, CeO_2, and other similar materials. Investigating the Zeta potential interaction mechanism between these particle pollutants and the epitaxial wafer can help to enhance the wafer cleaning effect. Figure 3 shows the Zeta potential of SiO_2, Al_2O_3, and CeO_2 measured by various researchers under different pH conditions[14-16].

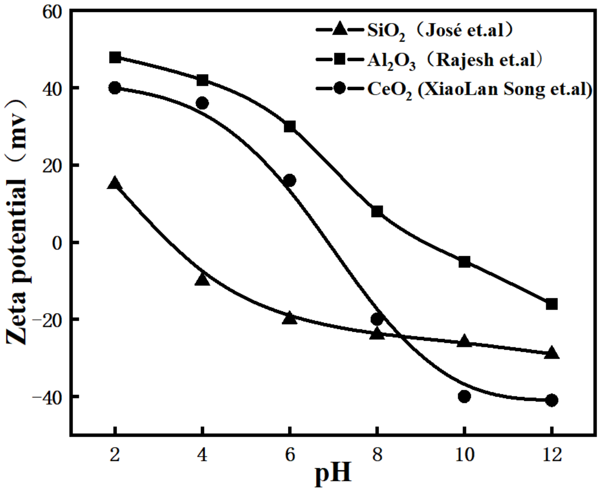


Figure 3. Zeta potential variation with pH for common contaminant particles

In Figure 3, it can be observed that when the pH value is 2, the Zeta potentials of the three types of particles are positive, while they are negative when the pH value is 12. This trend is similar to that observed for the Zeta potential changes of the PS spheres. However, in the SiC wafer cleaning process, the pH value of the SC1 cleaning solution is greater than 12, while that of the SC2 cleaning solution is less than 2. Hence, we hypothesize that the epitaxial wafer and the aforementioned contaminating particles possess differing Zeta potentials in the SC2 (acidic) cleaning solution, resulting in electrostatic attraction between the two. Although SC2 can remove metal ion contamination from the surface of the epitaxial wafer, it may increase the number of contaminating particles on the Si surface. Conversely, in the alkaline SC1 cleaning solution, both the epitaxial wafer Si surface and the aforementioned contaminating particles possess negative Zeta potentials, resulting in electrostatic repulsion between them. Therefore, the SC1 process can effectively remove contaminating particles from the Si surface. To verify this hypothesis, we conducted further experiments under the conditions presented in Table 1.

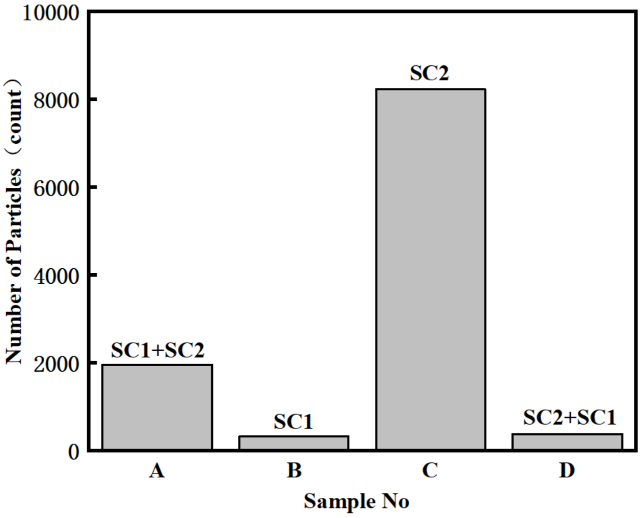


Figure 4. The number of remaining particles on each epitaxial wafer surface

In Figure 4, the number of residual particles on the Si surface for samples A-D was 1964, 324, 8231, and 385, respectively. The results indicate that samples B and D have the best particle removal effect on the Si surface, followed by sample A, while sample C has the poorest effect. Sample B only underwent the SPM and SC1 cleaning processes, whereas sample D had an additional SC2 process between SPM and SC1. The cleaning results show that the addition of an SC2 process hardly affects the particle removal effect of the SC1 process. Compared with sample A, which was processed by the traditional RCA process, sample D processed by the optimized process reduced surface particles by 80.4% and removed metal ion contamination. Sample C only underwent the SPM and SC2 cleaning processes, and the number of surface particles was significantly higher than that of the other three groups, which confirms Reinhardt's conjecture that SC2 is mainly used to remove metal ions. Additionally, comparing the number of residual particles on the Si surface of samples A and B shows that the SC2 process will increase the particle contamination on the epitaxial Si surface, which also confirms our aforementioned conjecture. From the above, it can be concluded that the cleaning process in the order of SPM-SC2-SC1 is beneficial for removing particle contamination on the epitaxial Si surface.

4. Summary

In this study, we have identified significant differences in the adsorption of PS spheres on SiC epitaxial wafers in acidic and alkaline solutions. By considering the principles of Zeta potential, we analyzed the charge status of the SiC epitaxial wafer Si surface at different pH values and compared it with the Zeta potential of common contaminants. The results revealed that Zeta potential plays a crucial role in the mechanism of particle adsorption on epitaxial wafers. Based on these findings, we optimized the SiC cleaning process and conducted experiments to validate its efficacy. The results of the experiments demonstrated that the SC2 cleaning process is not conducive to the removal of contamination particles on the Si surface, while the SC1 cleaning process can effectively remove surface particles on the epitaxial wafer and is not affected by other processes. Therefore, in practical industrial production, the adoption of the SPM-SC2-SC1 sequence cleaning process is beneficial for removing contamination particles on the SiC epitaxial wafer Si surface. If there is no metal ion contamination on the surface of the epitaxial wafer, the SC2 cleaning process can be omitted, which would reduce working time, chemical reagent usage, and the discharge of cleaning wastewater.

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