A Diamond Electrochemical Cleaning Technique for Organic Contaminants on Silicon Wafer Surfaces

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Abstract: Peroxodiphosphate anion (a powerful oxidant) can be formed in a special water-based cleaning agent through an electrochemical reaction on boron-doped diamond electrodes. This electrochemical reaction was applied during the oxidation, decomposition, and removal of organic contaminations on a silicon wafer surface, and it was used as the first step in the diamond electrochemical cleaning technique (DECT). The cleaning effects of DECT were compared with the RCA cleaning technique, including the silicon surface chemical composition that was observed with X-ray photoelectron spectroscopy and the morphology observed with atomic force microscopy. The measurement results show that the silicon surface cleaned by DECT has slightly less organic residue and lower micro-roughness, so the new technique is more effective than the RCA cleaning technique.

Key words: organic contaminations; silicon wafer surface cleaning; boron-doped diamond electrodes; powerful oxidant; micro-roughness; electrochemical cleaning

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1 Introduction

Organic pickup during IC processing is hard to avoid. The residual organic contaminants on silicon wafer surfaces are not only a result of the absorption of organic volatiles in the clean room air, but also the organic substances from various sources in the process environment, such as organic substances from cleaning solutions, plastic shippers, and chemicals used in the photolithographic process[1]. With the rapid increase of the density and the decrease of the feature size of ultra large-scale integrated circuits (ULSI), a trace amount of organic contaminants on silicon wafer surface will have an increasingly detrimental impact on the performance and the yield of a semiconductor device, including degradation of gate-oxide integrity (GOI) and deviation in the thicknesses of CVD films[2~4]. Therefore, it is extremely important to remove organic contaminants from silicon surfaces prior to device fabrication.

In the process of IC manufacturing, organic contaminations on silicon wafer surface are mainly removed through the oxygenolysis method caused by the oxidants in cleaning agents, such as Piranha (H_2SO_4/H_2O_2, 100 ~ 130℃) solution and SC-1 (NH_4OH/H_2O_2/H_2O, 65~80℃) solution, which are all components of RCA cleaning. However, the powerful corrosion of oxidations (H_2SO_4, H_2O_2) and volatilization of NH_4OH in RCA cleaning solutions induce dangerous operations, environment pollution, an increase of surface micro-roughness and unstable cleaning effects[5~7]. In recent years, some research institutes such as ASTEC (Germany)[8,9], Sony (Japan)[9,10], and Semitool (USA)[11] applied ozone (O_3, a powerful oxidant) to replace H_2SO_4 and H_2O_2 and realized an improved effect. However, the solubility of O_3 in water decreases as the temperature rises. In addition, because of the poor stability of O_3, the concentration of O_3 will also gradually diminish through decomposition. The oxidation intensity is related to the concentration of the oxidant, so the oxidation intensity is low and not easily controlled in these new techniques. In order to obtain stability and high performance for organic contaminations cleaning, new equipments and methods should be studied further.

2 Proposition of DECT

As mentioned above, many papers have evaluated more suitable powerful oxidants for the cleaning process, which includes characteristics such as: harmless to the environment and the operators, the same oxidbility as O_3 in water, better solubility than O_3, easily controlled, simple cleaning process, compatible with existing equipment, and low cost.

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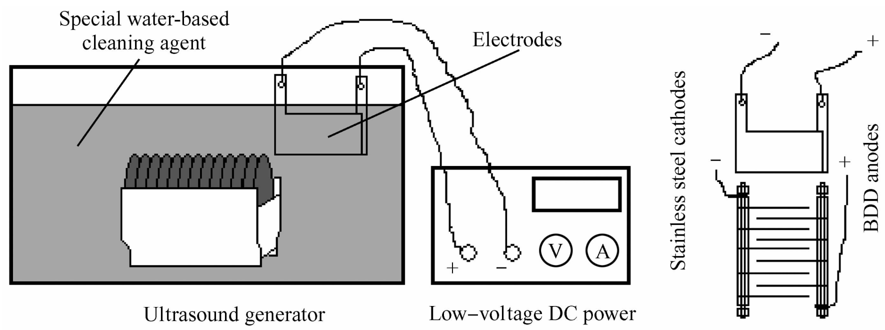

Fig. 1 Setup used in the first step and arrangement of BDD and stainless steel electrodes

According to Ref. [12], K_3PO_4 can produce high-purity peroxodiphosphate anion ($P_2O_8^{4-}$) based on the use of BDD electrodes, with a very high current efficiency, conversions over 90% and efficiencies over 60%. $P_2O_8^{4-}$ is an environmentally friendly reagent used in wastewater treatment. $P_2O_8^{4-}$ is also a strong oxidizing agent with a standard oxidation potential of 2.07V, so the oxidbility is as effective as O_3. In water solution, its solubility is much better than O_3, so it can easily oxidize and decompose the organics. The concentration of $P_2O_8^{4-}$, which is produced by the BDD electrodes, can be controlled through regulation of the voltage and current, and can be stable in a small range. As a new functional material, BDD electrodes show a higher chemical and electrochemical stability, a longer service lifetime, and less energy consumption. If BDD electrodes are used in the cleaning process, the cleaning agent can be recycled through the filter, so the cleaning cost is low.

Therefore, a DECT cleaning method was used and compared with RCA cleaning technique. The chemical composition on silicon surface was observed with XPS, and the morphology observed with AFM.

3 Experiments

3.1 DECT flow

The cleaning steps of DECT are shown in Table 1.

Table 1 Flow of DECT

Step	Operation	Solution or gas	Temperature /℃	Time /min
1	Cleaning	Special water-based cleaning agent	60	5
2	Spraying	DI-water	RT	3
3	Dipping	HF (4%wt)	RT	0.5
4	Spraying	DI-water	RT	3
5	Cleaning	Cleaning agent model FA/O-III	60	5
6	Spraying	DI-water	RT	2
7	Spraying	DI-water	70	2
8	Spraying	DI-water	RT	2
9	Dipping	HF (4%wt)	RT	0.5
10	Spraying	DI-water	RT	5
11	Drying	N_2	Above 100	1

In the first step, a special water-based cleaning agent is used as the electrolyte solution, which comprises 0.4mol/L solution of K_3PO_4 and the cleaning agent model FA/O-II produced by Hebei University of Technology. The pH value of the electrolyte solution is regulated to 12.00 ~ 12.25 with KOH, and the cleaning is carried out after warm-up for 1.5h with a voltage of about 8V. As the result, all kinds of organic contaminants can be removed. The cleaning agent model FA/O-III, used in the fifth step, comprises chelator invented by Professor Liu Yuling, and can remove the solid particles and metal ions, including K^+ from the first step. The resistivity of DI-water is 18MΩ·cm, and the other chemical reagents are all analytical reagents.

3.2 Setup used in the first step

The setup used in the first step is shown in Fig. 1. BDD electrodes provided by Tianjin University of Technology are used as anodes and stainless steel (AISI 304) as cathodes. The size of all electrodes is 55mm × 55mm, and the electrodes gap is 8mm. The power supply is low-voltage DC power. In order to increase the cleaning effects, ultrasonic waves were produced by a Kunshan Ultrasound Generator Model KQ500DE manufactured by Kunshan Ultrasound Equipment (China).

3.3 Experimental methods

Before cleaning, one n-type single-surface-polished Si (111) wafer was imaged by AFM. In order to simulate organic contaminations, the unpolished surface was covered with a high-temperature wax film used in CMP, and the polished surface was smeared with oil fingerprints. Then the chemical composition of the polished surface was observed with XPS. As samples, the silicon wafer was cut into six square chips (10mm × 10mm). The chips were randomly divided into two groups, and respectively cleaned by the RCA cleaning technique and by DECT. The chemical composition of the cleaned silicon surface was immediately

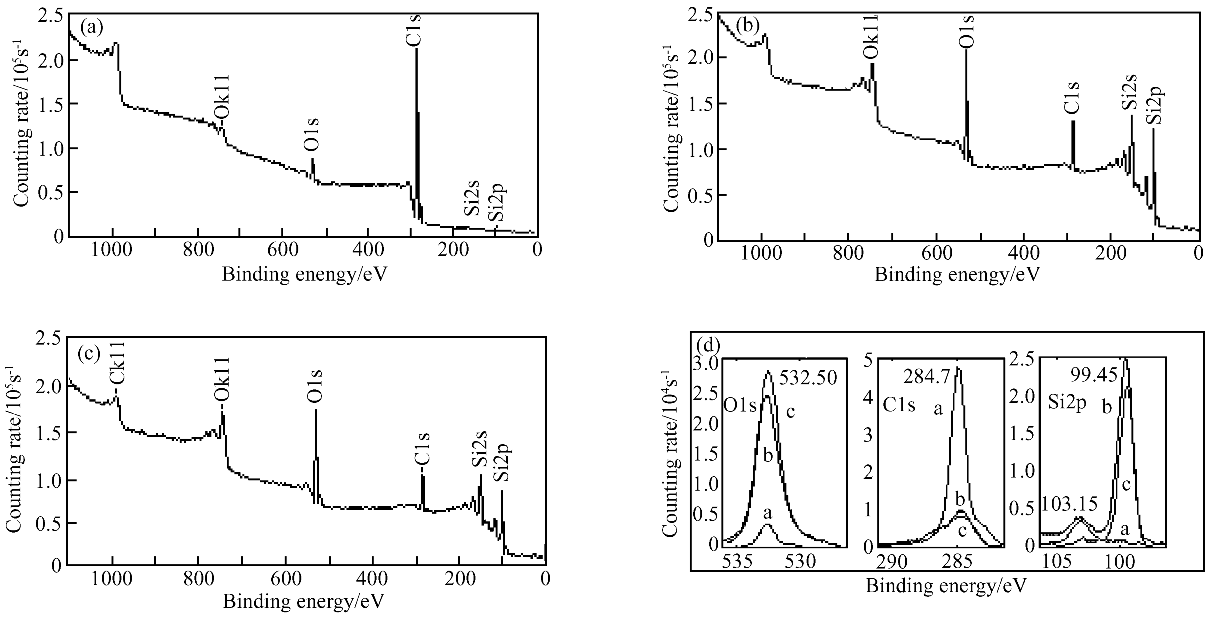

Fig. 2 Full and local scanning spectra of cleaned wafer surface by XPS (a) Before cleaning; (b) RCA cleaning technique; (c) DECT; (d) Three element local scanning spectra

observed with XPS, and the morphology was observed with AFM.

4 Results and discussion

4.1 XPS measurement

XPS measurement is the most important and effective method for observing the organic contaminations on the silicon surface, and it can directly reflect the quantity of organic residues according to measurement of the number of organic carbon atoms on the silicon surface[13]. Figure 2 shows the typical full and local scanning spectra of silicon surfaces, including the silicon wafer surface before cleaning and the silicon chips' surfaces cleaned by RCA cleaning technique and DECT.

The full scanning spectra show that the chemical compositions of the silicon surfaces are similar, and all three elements, oxygen, carbon and silicon, are present. Figure 2 (d) shows that the peak O1s at 532.50eV comes from oxygen bonded in Si-O of SiO_2; the peak C1s at 284.7eV comes from carbon bonded in C-C and C-H of organic contaminations[14]; the peak Si2p at 103.15eV comes from silicon bonded in Si-O of SiO_2, and the peak Si2p at 99.45eV comes from silicon bonded in Si-Si of crystal Si. In order to determine the effects of cleaning techniques, the organic carbon concentration must go through the integral of the three element local scanning spectra. The respective concentration percentages of three elements are shown in Table 2.

The measurement results show that the silicon surface before cleaning is mainly covered by organic contaminations, and the silicon chips' surfaces cleaned by two techniques all have trace organic carbon residues and a thin SiO_2 oxide layer. According to the comparison of the three elements' concentrations in Table 2, the silicon surface cleaned by DECT has slightly less organic residues than that by the RCA cleaning technique. Therefore, with respect to removing the organic contaminants from the silicon surface, the new technique is as effective as the RCA cleaning technique, or even better than the RCA cleaning technique.

4.2 AFM measurement

As mentioned above, the SC-1 treatment can cause silicon surface roughness that will degrade the dielectric properties of thin gate oxide film. In order

Table 2 Elements on wafer surface and their concentrations

Element concentration	Before	RCA cleaning technique				DECT			
/%	cleaning	1	2	3	Average	1	2	3	Average
O1s	6.75	33.25	31.48	34.18	32.97	32.11	34.97	35.37	34.15
C1s	92.81	28.72	29.31	23.16	27.06	26.81	23.71	22.00	24.17
Si2p	0.45	38.03	39.21	42.66	39.97	41.08	41.32	42.63	41.68

Table 3 Morphology parameters and the values for different silicon surfaces

Parameter	Before cleaning		RCA cleaning technique				DECT			
	Sample	Average	Sample			Average	Sample			Average
			1	2	3		1	2	3	
Image Z range /nm	2.622		16.253	17.791	15.098		6.481	6.748	6.290	
	2.676	2.665	16.420	17.265	17.681	16.715	6.822	6.243	6.920	6.650
	2.698		16.214	16.928	16.786		6.995	6.724	6.625	
RMS/nm	0.211		0.931	0.976	0.893		0.403	0.414	0.395	
	0.215	0.214	0.936	0.958	0.970	0.942	0.417	0.393	0.421	0.410
	0.217		0.917	0.951	0.944		0.424	0.413	0.408	

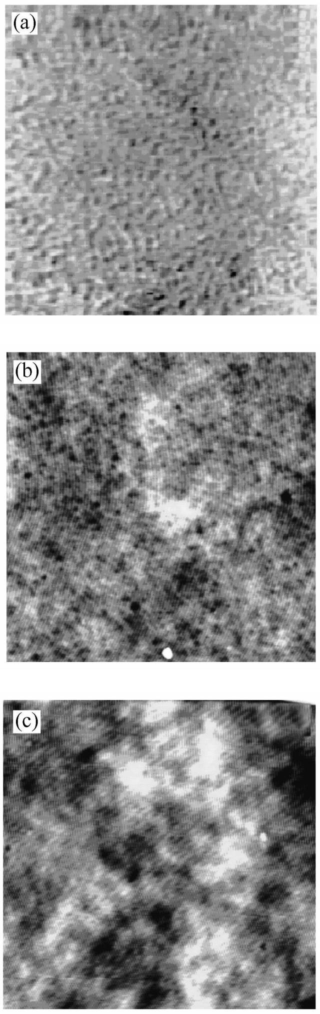

Fig.3 AFM photograph of cleaned wafer surface (a) Before cleaning;(b) RCA cleaning technique;(c) DECT

to check whether there is the same problem with the new cleaning technique, the morphology can be observed with AFM. Figure 3 shows the typical AFM photograph of silicon surfaces, including the silicon wafer surface before cleaning and the silicon chips' surfaces cleaned by the RCA cleaning technique and DECT.

According to the AFM photograph over a 5μm×5μm area, the silicon wafer before cleaning has an atomically flat silicon surface. The silicon chip surface cleaned by the RCA cleaning technique has a large number of etch pits, but the one cleaned by DECT has few etch pits. The image Z range and root mean square (RMS) roughness are used to characterize the morphology of the silicon surface, and the respective values of the two morphology parameters are shown in Table 3. The micro-roughnesses of the cleaned silicon surfaces all increased, but the silicon chips cleaned by DECT has a lower micro-roughness than that by the RCA cleaning technique. Therefore, with respect to retaining the silicon surface morphology, the new cleaning technique is more effective than the RCA cleaning technique.

5 Conclusion

The cleaning effects of DECT are compared with the RCA cleaning technique, including the silicon surface chemical composition observed with XPS and the morphology observed with AFM. The measurement results show that the silicon surface cleaned by DECT has slightly less organic residues and lower micro-roughness. Therefore, with respect to removing the organic contaminants from the silicon surface, the new technique is as effective as the RCA cleaning technique, or even better than the RCA cleaning technique. With respect to retaining the silicon surface morphology, the new cleaning technique is more effective than the RCA cleaning technique.

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金刚石膜电化学清洗硅片表面有机沾污的研究

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摘要: 采用金刚石膜电极的电化学方式在专用水基清洗剂中不断产生强氧化剂过氧焦磷酸根离子($P_2O_8^{4-}$),并将此方式作为金刚石膜电化学清洗工艺步骤的第一步,用于氧化去除硅片表面的有机沾污. 通过与 RCA 清洗进行对比实验,并应用 X 射线光电子谱和原子力显微镜进行清洗效果的检测,结果表明,本清洗工艺处理后的硅片表面有机碳含量更少,微粗糙度小,明显优于现有的 RCA 清洗工艺.

关键词: 有机沾污; 硅片表面清洗; 掺硼金刚石膜电极; 强氧化剂; 微粗糙度; 电化学清洗
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