A new cleaning process combining non-ionic surfactant with diamond film electrochemical oxidation for polished silicon wafers

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Abstract: This paper presents a new cleaning process for particle and organic contaminants on polished silicon wafer surfaces. It combines a non-ionic surfactant with boron-doped diamond (BDD) film anode electrochemical oxidation. The non-ionic surfactant is used to remove particles on the polished wafer's surface, because it can form a protective film on the surface, which makes particles easy to remove. The effects of particle removal comparative experiments were observed by metallographic microscopy, which showed that the 1% v/v non-ionic surfactant achieved the best result. However, the surfactant film itself belongs to organic contamination, and it eventually needs to be removed. BDD film anode electrochemical oxidation (BDD-EO) is used to remove organic contaminants, because it can efficiently degrade organic matter. Three organic contaminant removal comparative experiments were carried out: the first one used the non-ionic surfactant in the first step and then used BDD-EO, the second one used BDD-EO only, and the last one used RCA cleaning technique. The XPS measurement result shows that the wafer's surface cleaned by BDD-EO has much less organic residue than that cleaned by RCA cleaning technique, and the non-ionic surfactant can be efficiently removed by BDD-EO.

Key words: non-ionic surfactant; BDD film anode; electrochemical oxidation; cleaning
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1. Introduction

The cleaning technique is one of the key points in the manufacture of micro-electronics devices. In the micro-electronics field, the RCA cleaning technique is widely used to remove the bulk of contaminants on silicon wafer surfaces. However, the manufacturing process of silicon is becoming more and more sophisticated, and the cleaning progress has many repeat steps in the integrated circuit chip production. For example, there are more than 80 cleaning processes in the GLSI production, and the consumption of chemical reagents such as HCl and H_2O_2 is high. It should be reduced in order to protect the environment and cut down the cost. At present, one new cleaning technique is the ozone cleaning spray technique. It has fewer cleaning steps and lower consumption of chemical reagents compared to traditional cleaning techniques, and it can achieve better cleaning results. On the basis of the technique using ozone, a new cleaning process combining non-ionic surfactant with boron-doped diamond (BDD) film anode electrochemical oxidation is introduced in this paper, which is an efficient and environmentally friendly cleaning technique.

1.1. BDD film anode electrochemical oxidation

In recent years, due to its capabilities in the electrochemical field, such as very high electrochemical stability, low background current[1,2], high current efficiency of the oxidation process[3], and wide potential electrochemical window, BDD film anode has been successfully applied to analysis of electrical, electrochemical degradation of organic waste water and preparation of technology-oxidants[4,5]. It is regarded as the most promising electrode material, and has become a focus of the study of electrochemical application.

BDD film anode can degrade organic matter and prepare oxidants[6], because it has a very wide potential electrochemical window compared with other electrode materials, up to more than 3.5 V. With high oxygen evolution potential, it can generate a large number of oxidation of hydroxyl radicals on the anodic surface. Ozone and peroxides, such as hydrogen peroxide and pyrophosphate peroxide, can also be prepared by BDD film anode electrochemical oxidation (BDD-EO)[7], and are steadier than free radicals and have a longer survival time in solution and strong oxidation ability. Organic compounds in solution can be oxidized not only directly on the surface of the BDD film anode, but also indirectly by hydroxyl radicals and other oxidizing agents. Because of the electrochemical stability of BDD film anode, it can be used for a very long time, and the chemical reagents in BDD-EO are in small amounts and can be reused. So BDD-EO is an environmentally friendly cleaning technique.

1.2. Non-ionic surfactant

The non-ionic surfactant can efficiently remove particles on surfaces, because it can significantly reduce the surface tension of the liquid and interfacial tension. The non-ionic surfactant molecule has two parts, hydrophilic and hydrophobic. Fatty alcohol-polyoxyethylene ether, a kind of non-ionic surfactant, is selected in the experiment. This non-ionic surfactant cannot be ionized, so it will not bring ionic contaminants. Fur-

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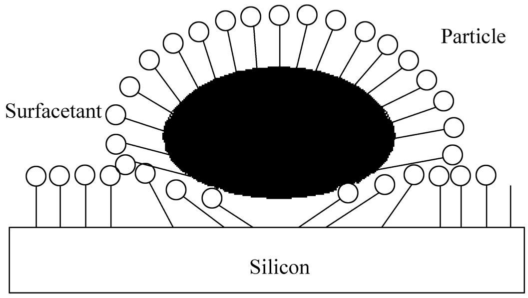

Fig. 1. Non-ionic surfactant film adsorption on the silicon surface and around a particle.

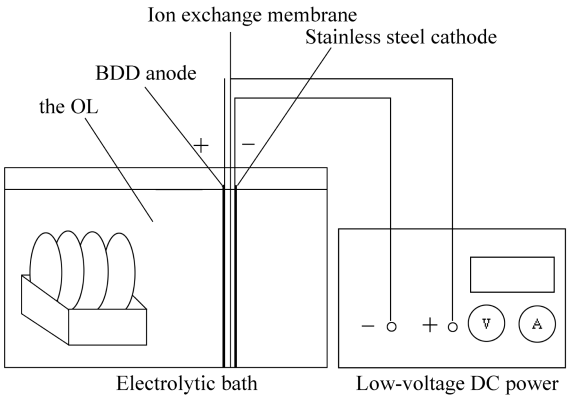

Fig. 2. Setup of the BDD film anode electrochemical oxidation.

thermore, it has a strong osmotic force, which can deeply penetrate and "wedge". The length of the hydrophilic part is more than two thirds, so that it forms a thick cover layer. The non-ionic surfactant molecules can adsorb on the silicon wafer's surface and around particles, which hold up particles, and form an adsorption layer around the particles, to prevent adsorption of particles on the surface[8], as shown in Fig. 1.

The non-ionic surfactant can form a protective layer film on the polished silicon wafer, which can effectively control the adsorption of particles, keeping adsorbates in the physical adsorption state, making them easy to remove. However, this layer of protective film itself belongs to the organic contamination, and eventually needs to be removed. When combining the non-ionic surfactant with BDD-EO, it can remove both organic and particle contaminants at the same time, as well as the adsorbed non-ionic surfactant on the surface.

2. Experiments

In the experiments, the oxidizing agent in the electrolyte produced by BDD-EO is called the oxidizing liquid (OL for short). The experimental setup of preparing the OL is shown in Fig. 2. It is a two-box electrolytic bath, which is partitioned by the ion exchange membrane, and the anode bath is larger, for preparing the OL and cleaning wafers. The solution in the anode bath is 0.4 mol/L monopotassium phosphate, and in the cathode bath is a solution of potassium hydroxide, whose pH is 12.0. All of the electrolyte was prepared by deionized water, whose electrical resistivity is 18 MΩ·cm. The power supply is low voltage DC power, and the voltage is 8–12 V. Incidentally, the contaminant of K^+ in the OL can be removed by the following step, which is not mentioned in this paper[9].

Before the experiments, all the wafers were polished by the chemical–mechanical polishing (CMP) technique, and the OL needs to be prepared and heated to 70 ℃ by on load voltage of about 10 V for 1.5 h.

2.1. Particle removal comparative experiments

(1) A polished wafer was put in the OL for 10 min, then it was taken out of the anode bath and put into a container full of the OL, and then the container was put into a supersonic cleaner at a frequency of 80 kHz for 10 min. After that, it was cleaned three times in another container, which was full of fresh deionized water and put into a supersonic cleaner at a frequency of 80 kHz for 10 min each time. In the last step, it was dried in nitrogen atmosphere.

(2) Two wafers were each soaked into a container of the 1% v/v non-ionic surfactant and a container of the 10% v/v non-ionic surfactant; each wafer was soaked for 20 min at room temperature, and then the containers were put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Then each wafer was cleaned three times in another container, which was full of fresh deionized water and put into a supersonic cleaner at a frequency of 80 kHz for 10 min each time. In the last step, each wafer was dried in nitrogen atmosphere.

The cleaned wafers were observed by metallographic microscopy under the overall situation with 500 times magnification. The results and discussion are given in Section 3.1.

2.2. Organic matter removal comparative experiments

The electrochemical oxidation of BDD film anode can produce high-intensity oxidizing agents in the electrolyte. The oxidizing agents are not only able to effectively remove the organic contaminants on the surface, but also the non-ionic surfactant. Comparative experiments were carried out to verify the effect of organic matter removal.

(1) Non-ionic surfactant-OL cleaning (S-OL cleaning for short)

At room temperature, a polished wafer was soaked in a container of 1% v/v non-ionic surfactant for 20 min, and then the container was put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Then the wafer was put in the OL for 10 min; after that it was taken out of the anode bath and put into a container full of the OL, and then the container was put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Then it was cleaned three times in another container, which was full of fresh deionized water and put into a supersonic cleaner at a frequency of 80 kHz for 10 min each time. In the last step, it was dried in nitrogen atmosphere.

(2) OL cleaning

A polished wafer was put in the OL for 10 min, then it was taken out of the anode bath and put into a container full of the OL, and then the container was put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Then the wafer was cleaned three times in another container, which was full of fresh deionized water and put into a supersonic cleaner at a frequency of 80 kHz for 10 min each time. In the last step, it was dried in nitrogen atmosphere.

(3) Traditional RCA cleaning

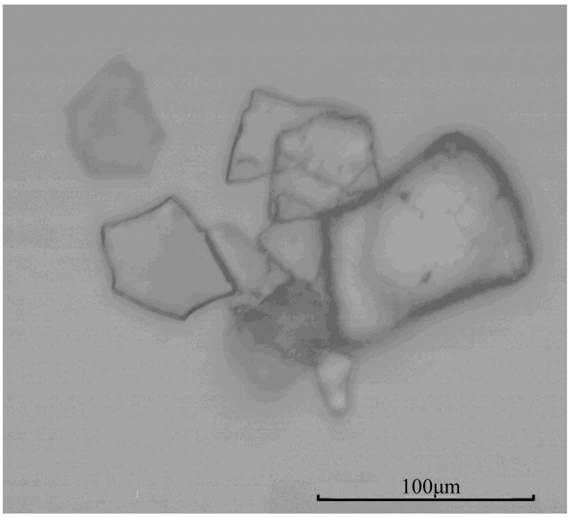

Fig. 3. Sheet micelles observed with 500 times magnification.

Table 1. Statistics of the particle number on the wafer's surface.

Particle removal comparative experiment	Particle number
1. OL cleaning	58
2. 1% v/v non-ionic surfactant	24
3. 10% v/v non-ionic surfactant	67

A wafer was put in the RCA (SC1), where the volume inverse proportion of NH_4OH (29%), H_2O_2 (30%) and H_2O was 1 : 1 : 5, at a temperature of 80 °C, for 10 min, and then put into a supersonic cleaner at a frequency of 80 kHz for 10 min. After that it was put in the RCA (SC2), where the volume inverse proportion of HCl, H_2O_2 and H_2O was 1 : 1 : 6, at a temperature of 70 ℃, for 10 min, and then put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Then the wafer was cleaned three times in another container , which was full of fresh deionized water and put into a supersonic cleaner at a frequency of 80 kHz for 10 min each time. In the last step, it was dried in nitrogen atmosphere.

All the experimental wafers were dried in nitrogen atmosphere, put into clean glassware, and sealed in numbered boxes filled with nitrogen. Then the boxes were sent to the examination center for testing of the organic content with X-ray photoelectron spectroscopy (XPS), and the test results are given in Section 3.2.

3. Results and discussion

3.1. Metallographic microscope measurement

The cleaned wafers were observed by metallographic microscopy under the overall situation with 500 times magnification. The statistics of the particle number is shown in Table 1.

The effect of particle removal with cleaning by 1% v/v non-ionic surfactant is obviously better than that with OL cleaning and 10% v/v non-ionic surfactant. Because of the high concentration, the 10% v/v non-ionic surfactant produced micelles in the solution as well as on the wafer's surface. The sheet micelles produced by the 10% v/v non-ionic surfactant are shown in Fig. 3. Therefore, when using non-ionic surfactant, it should be at an appropriate concentration. So in the organic matter removal comparative experiments, the concentration of non-ionic surfactant is 1% v/v.

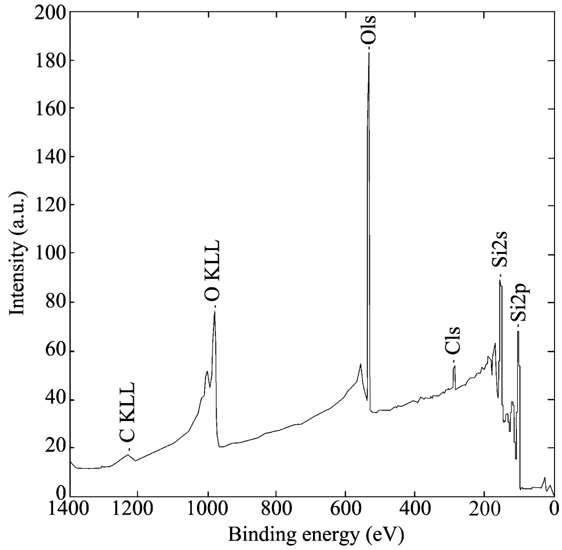

Fig. 4. XPS of wafers cleaned by the S-OL cleaning technique.

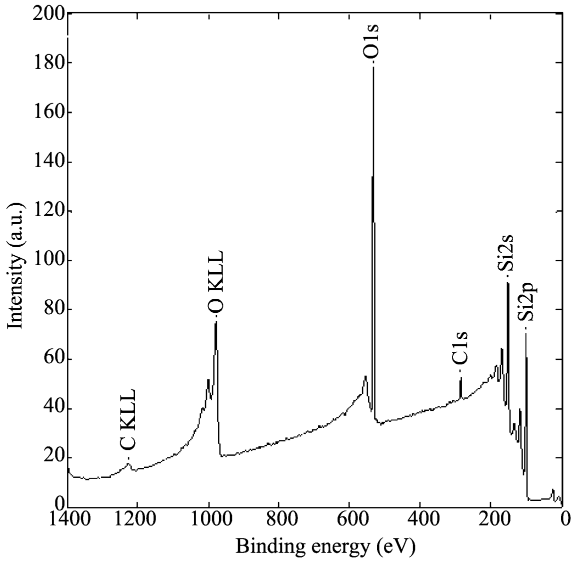

Fig. 5. XPS of wafers cleaned by the OL cleaning technique.

3.2. XPS measurement

XPS measurement is an important and effective method of observing organic contaminants on a wafer's surface. It can directly reflect the quantity of organic residues according to measurement of the number of organic carbon atoms on the wafer's surface[10]. Figures 4–7 show typical full and local scanning spectra of the wafers' surfaces, cleaned in the three organic matter removal comparative experiments.

The full scanning spectra show that the chemical compositions of the silicon surfaces are basically three elements, oxygen, carbon and silicon. The peak O1s is from oxygen bonded in Si–O of SiO_2; the peak C1s at 284.7 eV comes from carbon bonded in C–C and C–H of organic contaminants[11]; the peak

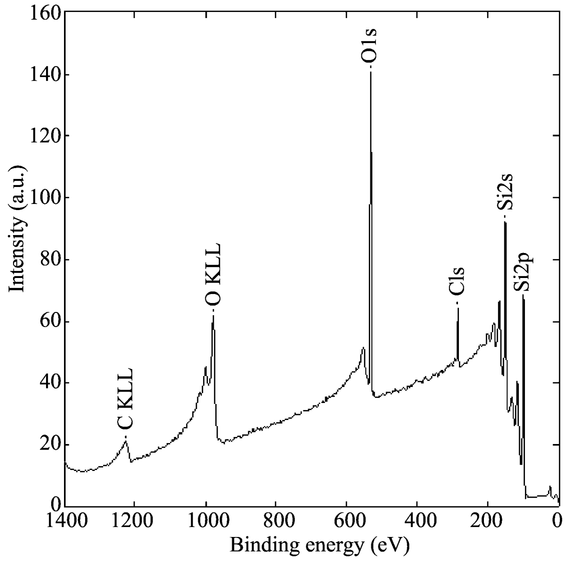

Fig. 6. XPS of wafers cleaned by the traditional RCA cleaning technique.

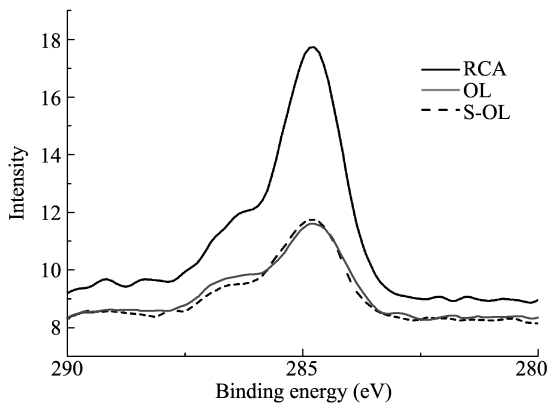

Fig. 7. Local scanning of C1s by XPS wafers cleaned by the three cleaning techniques.

Table 2. Relative atomic percentage content (atm.%) of elements on wafers cleaned by different techniques.

Element	S-OL	OL	RCA
C1s	7.3	7.34	18.02
O1s	46.83	46.33	37.29
Si2p	45.87	46.32	44.68

Si2s is from silicon bonded in Si–O of SiO_2, and the peak Si2p is from silicon bonded in Si–Si of crystalline Si. The respective concentration percentages of the three elements are shown in Table 2.

The measurement results show that the silicon wafers cleaned by the three 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 wafers' surfaces cleaned by the OL and the S-OL cleaning techniques have much fewer organic residues and a thicker oxide layer than that using the RCA cleaning technique. Therefore, with respect to removing organic contaminants from the wafer surface, the new technique is better than the RCA cleaning technique.

4. Conclusion

The new cleaning technique combining non-ionic surfactant with BDD film anode electrochemical oxidation can remove organic and particle contaminants at the same time, as well as the adsorbed surfactant on the wafer's surface. The chemical reagent in BDD-EO is in small amounts and can be reused; furthermore, HCl, NH_4OH and H_2O_2 are not used in the S-OL cleaning technique. So the S-OL cleaning technique is an environmentally friendly cleaning technique.

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