A new cleaning process for the metallic contaminants on a post-CMP wafer's surface*

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Abstract: This paper presents a new cleaning process using boron-doped diamond (BDD) film anode electrochemical oxidation for metallic contaminants on polished silicon wafer surfaces. The BDD film anode electrochemical oxidation can efficiently prepare pyrophosphate peroxide, pyrophosphate peroxide can oxidize organic contaminants, and pyrophosphate peroxide is deoxidized into pyrophosphate. Pyrophosphate, a good complexing agent, can form a metal complex, which is a structure consisting of a copper ion, bonded to a surrounding array of two pyrophosphate anions. Three polished wafers were immersed in the 0.01 mol/L $CuSO_4$ solution for 2 h in order to make comparative experiments. The first one was cleaned by pyrophosphate peroxide, the second by RCA (Radio Corporation of America) cleaning, and the third by deionized (DI) water. The XPS measurement result shows that the metallic contaminants on wafers cleaned by the RCA method and by pyrophosphate peroxide is less than the XPS detection limits of 1 ppm. And the wafer's surface cleaned by pyrophosphate peroxide is more efficient in removing organic carbon residues than RCA cleaning. Therefore, BDD film anode electrochemical oxidation can be used for microelectronics cleaning, and it can effectively remove organic contaminants and metallic contaminants in one step. It also achieves energy saving and environmental protection.

Key words: diamond film; cleaning; metallic contaminant; pyrophosphate
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1. Introduction

1.1. Metallic contaminants

The dual-Damascene process is widely used nowadays in the semiconductor industry[1]. In this process, copper has progressively replaced aluminum for the fabrication of interconnections in integrated circuits (ICs)[2]. This switch emerged due to copper's advantageous characteristics, such as low resistivity and high immunity to electro-migration, which in turn results in greater circuit reliability and markedly higher clock frequency. Chemical–mechanical planarization (CMP) has become an essential step in Damascene processing of copper interconnect structures[3]. CMP has many advantages, including surface planarization, reduced process steps and thermal budget[4,5]. However, it will induce metal and organic contamination residues on the dielectric material surface. The control of metallic residues after CMP is getting more emphasis in advanced interconnects. Cleaning efficiency and the removal of metallic contaminations have a significant impact on productivity and reliability. A major reliability issue is dielectric degradation caused by Cu-ion drift. Because of its quick diffusion through SiO_2 and Si, and the formation of acceptor and donor levels within the forbidden band-gap, Cu needs to be cleaned after the CMP process[6].

Metallic contaminants can be removed by a metal complex, which is a structure consisting of a central atom or ion (usually metallic) bonded to a surrounding array of complexing agents and chelating agents. An organic compound ethylenediaminetetraacetic acid (EDTA) and several salts, such as disodium EDTA, are used to remove metallic contaminants because of its role as a chelating agent[7]. However, EDTA is classed as an organic contaminant, and eventually needs to be removed.

1.2. BDD film anode electrochemical oxidation

In recent years, due to the capability of BDD film anodes in the electrochemical field, such as very high electrochemical stability, low background current[8,9], high current efficiency of the oxidation process[10], and wide potential electrochemical window, it has been successfully applied to the analysis of electrical and electrochemical degradation of organic waste water and preparation of technology-oxidants[11,12]. It is regarded as the most promising electrode material, and it has become the focus in the study of electrochemical application.

BDD film anodes can degrade organic matter and prepare oxidants[13] because it has a very wide potential electrochemical window compared with other electrode materials, up to more than 3.5 V. With a high oxygen evolution potential, the BDD film anode can electrochemically oxidize the phosphate to pyrophosphate peroxide. The reaction formula is shown in Eq. (1). Organic compounds in solution can be oxidized by pyrophosphate peroxide, and this is deoxidized into pyrophosphate, as shown in Eq. (2).

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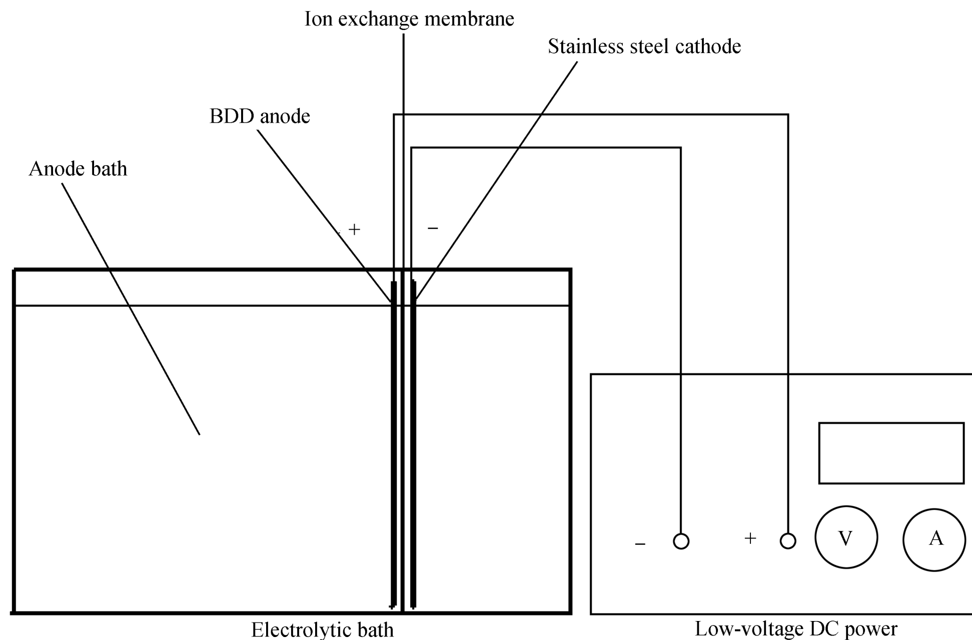
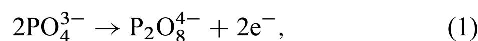
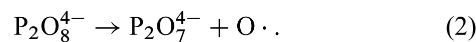


Fig. 1. Setup for BDD film anode electrochemical oxidation.

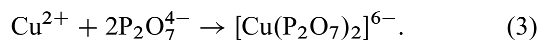


$$2PO_4^{3-} \rightarrow P_2O_8^{4-} + 2e^-, \quad (1)$$



$$P_2O_8^{4-} \rightarrow P_2O_7^{4-} + O\cdot. \quad (2)$$

Pyrophosphate is a kind of good complexing agent and has many uses in industrial chemistry. For example, potassium pyrophosphate (KPP) can form a metal complex, which is a structure consisting of a copper ion, bonded to a surrounding array of two pyrophosphate anions, as shown in Eq. (3):



$$Cu^{2+} + 2P_2O_7^{4-} \rightarrow [Cu(P_2O_7)_2]^{6-}. \quad (3)$$

This paper presents a new cleaning method to remove metal ion contaminants. BDD film anode electrochemical oxidation is used to prepare pyrophosphate peroxide, the pyrophosphate peroxide can be deoxidized into pyrophosphate, and the pyrophosphate is able to control the metal ion contaminants on the wafer's surface.

2. Experiments

2.1. Setup

Figure 1 shows the experimental setup for preparing pyrophosphate peroxide. It is a two-box electrolytic bath, which is partitioned by the ion exchange membrane, and the anode bath for preparing pyrophosphate peroxide is larger. The solution in the anode bath is 0.4 mol/L monopotassium phosphate, and in the cathode bath it is potassium hydroxide, which has a pH of 12.0. All of the electrolytes are prepared with DI water (the resistivity of the DI water is 18 MΩ·cm). The power supply is low voltage direct current (DC) power, and the voltage is 8–12 V. The pyrophosphate peroxide needs to be prepared by supplying power on load voltage of about 8 V for 3 h.

2.2. Comparative experiments

In this work, we prepared three polished wafers for the comparative experiments. All three wafers were polished by the chemical mechanical polishing (CMP) technique. In order to obtain the metal ion polluted wafers, the polished wafers were immersed in a solution of 0.01 mol/L $CuSO_4$ for 2 h, and then cleaned by three methods, as follows.

2.2.1. KPP cleaning

A polished wafer was immersed in pyrophosphate peroxide solution for 10 min, and then rinsed with fresh DI water. After that the wafer was ultrasonically cleaned at a frequency of 80 kHz for 10 min. In the final step, the wafer was dried in a nitrogen atmosphere.

2.2.2. Traditional RCA cleaning

The second wafer was immersed for 10 min in RCA (SC1) solution (NH_4OH (29%) : H_2O_2 (30%) : H_2O in a volume ratio of 1 : 1 : 5) at a temperature of 80 ℃. After ultrasonic cleaning at a frequency of 80 kHz for 10 min, the wafer was immersed in RCA (SC2) solution (HCl (37%) : H_2O_2(30%) : H_2O in a volume ratio of 1 : 1 : 6) at a temperature of 70 ℃, for 10 min. Then the wafer was ultrasonically cleaned at a frequency of 80 kHz for 10 min after rinsing with DI water. In the final step, the wafer was dried in a nitrogen atmosphere.

2.2.3. DI water cleaning

The third wafer was put into a container full of fresh DI water, and then the container was put into a supersonic cleaner at a frequency of 80 kHz for 10 min. Finally, it was dried in a nitrogen atmosphere.

3. Results and discussion

Investigations by means of X-ray photoelectron spectroscopy (XPS) were performed to analyze the surface. After N_2 drying, all the experimental samples were immediately loaded into the XPS loading lock and then transferred to the

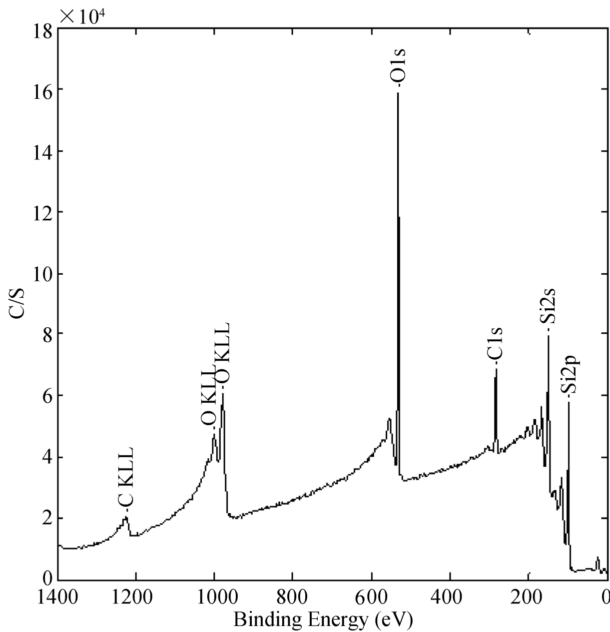


Fig. 2. XPS of wafer cleaned by DI water.

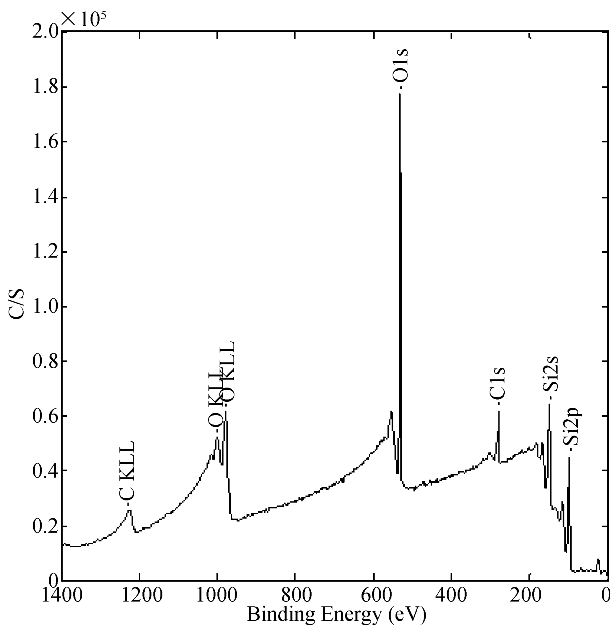


Fig. 3. XPS of wafer cleaned by the RCA cleaning technique.

main chamber. The results of the XPS analysis are reported in the followed figures.

XPS measurement is an important and effective method to observe elements on a surface, and detections limits of parts per million (ppm) are possible[10]. XPS measurement can therefore be used to observe the copper contaminants on a wafer's surface. Figures 2–4 show the typical full scanning spectra of the three wafer surfaces, and Figure 5 shows the local scanning spectra of Cu2p3. XPS full scanning spectra of the surface shows that the chemical composition of the silicon surfaces are basically three elements: oxygen, carbon and silicon. However, copper cannot be displayed in the typical full scanning spectra, due to it belonging to a pollution of trace elements, so it can

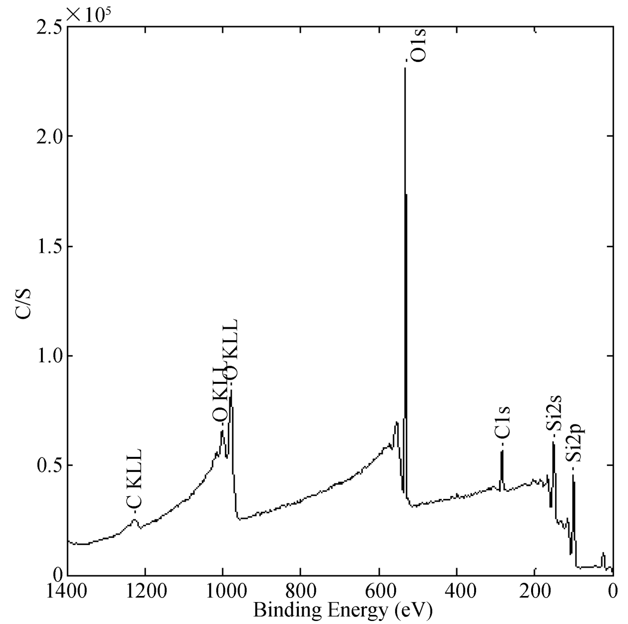


Fig. 4. XPS of wafer cleaned by the KPP cleaning technique.

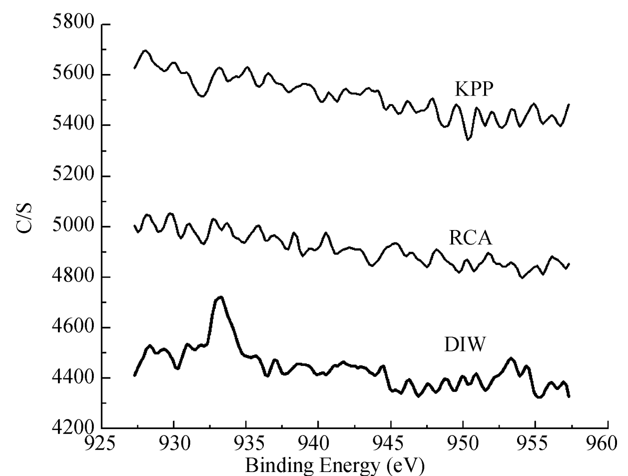


Fig. 5. Local scanning of Cu2p3 by XPS wafers cleaned by the three cleaning techniques.

Table 1. Relative atomic percentage content (atm.%) of elements on wafers cleaned by different techniques.

Element	DI water cleaning	KPP cleaning	RCA cleaning
Cu2p3	0.06	0.00	0.00
C1s	20.25	10.13	18.28
O1s	40.22	53.18	41.13
Si2p	39.46	36.13	39.59

only be seen in the local scanning spectra. The XPS analysis results in Fig. 5 show that only the wafer without cleaning has a clear peak, and the wafers cleaned by RCA cleaning and KPP have no peak in the local scanning spectra. So we can conclude that, in terms of metallic contaminant removal, KPP can reach the level of RCA cleaning, and both of the techniques provide a detection limit of less than 1 ppm.

The results of relative atomic percentage content of elements are shown in Table 1. As can be seen, the relative atomic

percentage content of copper is 0.00 after KPP and RCA cleaning. This indicates that both techniques can completely remove the copper ion. However, Table 1 also shows that the relative atomic percentage content of carbon obtained with KPP cleaning is much lower than RCA cleaning. Thus, we have to consider that KPP is more efficient in removing organic carbon residues than the RCA cleaning. KPP cleaning is more efficient because potassium pyrophosphate peroxide oxidized organic contaminants, and at the same time it was deoxidized into potassium pyrophosphate, which formed a metal complex to remove the copper contaminant.

4. Conclusion

BDD film anode electrochemical oxidation can efficiently prepare pyrophosphate peroxide, pyrophosphate peroxide can oxidize organic contaminants[14], and pyrophosphate peroxide is deoxidized into pyrophosphate. Pyrophosphate, a kind of good complexing agent, is able to control metal ion contaminants on a wafer's surface. Therefore, BDD film anode electrochemical oxidation can be used for microelectronics cleaning, and it can effectively remove organic contaminants and metallic contaminants in one step. It also achieves energy saving and environmental protection.

References

[1] Gutmann R J, Chow T P, Lakshminarayanan S, et al. Integration of copper multilevel interconnects with oxide and polymer interlevel dielectrics. Thin Solid Films, 1995, 270: 472

[2] Hau-Riege C S. An introduction to Cu electromigration. Microelectron Reliab, 2004, 44: 195

[3] Beverina A, Bernard H, Palleau J, et al. Copper photocorrosion phenomenon during post CMP cleaning. Electrochem Solid State Lett, 2000, 3 (3): 156

[4] Steigerwald J M, Murarka S P, Duquette D J, et al. Surface layer formation during the chemical mechanical polishing of copper thin films. Proceedings of the Symposium on Technology and Manufacturability of Material Research Society, Pittsburgh, PA, USA, 1994: 133

[5] Steinbruchel C. Patterning of copper for multilevel metallization: reactive ion etching and chemical mechanical polishing. Appl Surf Sci, 1995, 91: 139

[6] Joly J P. Metallic contamination assessment of silicon wafers. Microelectron Eng, 1998, 40: 285

[7] Ernst E. Chelation therapy for peripheral arterial disease: a systematic review. Circulation, 1997, 96(3): 1931

[8] Saha M S, Furuta T, Nishiki Y. Electrochemical synthesis of sodium peroxycarbonate at boron-doped diamond electrodes. Electrochemical and Solid-State Lett, 2003, 6(7): D5

[9] Sarada B V, Rao T N, Tryk D A, et al. Electrochemical characterization of highly boron-doped diamond microelectrodes in aqueous electrolyte. Journal of the Electrochemical Society, 1999, 146(4): 1469

[10] Saha M S, Furuta T, Nishiki Y, et al. Conversion of carbon dioxide to peroxycarbonate at boron-doped diamond electrode. Electrochem Commun, 2004, 6: 201

[11] Gandini D, Mahe E, Michaud P A, et al. Oxydation of carboxylic acid at boron-doped diamond electrodes. J Appl Electrochem, 2000, 30: 1345

[12] Panizza M, Duo I, Michaud P A, et al. Electrochemical generation of silver (II) at boron-doped diamond electrodes. Electrochemical and Solid-State Lett, 2000, 3(12): 550

[13] Michaud P A, Mahe E, Haenni W, et al. Preparation of peroxodisulfuric acid using boron-doped diamond thin film electrodes. Electrochemical and Solid-State Lett, 2000, 3(2): 77

[14] Zhang Jianxin, Liu Yuling, Tan Baimei, et al. A diamond electrochemical cleaning technique for organic contaminants on silicon wafer surfaces. Journal of Semiconductors, 2008, 29(3): 473