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Evaluation of Citric Acid Added Cleaning Solution for Removal of Metallic Contaminants on Si Wafer Surface

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Abstract−We have investigated cleaning solutions based on citric acid (CA) to remove metallic contaminants from the silicon wafer surface. Silicon wafers were intentionally contaminated with Fe, Ca, Zn, Na, Al and Cu standard solution by spin coating method and cleaned in various CA-added cleaning solutions. The concentration of metallic contaminants on the silicon wafer surface before and after cleaning was analyzed by vapor phase decomposition/inductively coupled plasma-mass spectrometry (VPD/ICP-MS). And the surface micro-roughness was also measured by atomic force microscopy (AFM) to evaluate the effect of cleaning solutions. It was found that acidic CA/H_2O solution has the ability to remove metallic contaminants from silicon surfaces. Fe, Ca, Zn and Na on silicon surface were decreased from the order of 10^{12} atoms/cm^2 to the order of 10^9 atoms/cm^2 even at low CA concentration, low temperature of CA solution and with short immersion time. CA was also effective in alkali cleaning solution. Fe, Ca, Zn, Na and Cu were reduced down to the order of 10^9 atoms/cm^2 in CA added with $NH_4OH/H_2O_2/H_2O$ solution without degradation of surface micro-roughness.

Key words: Citric Acid, Si Wafer, Metallic Contaminants, Vapor Phase Decomposition

INTRODUCTION

As requirements for the contaminants in the ultra large scale integrated (ULSI) device process become more stringent, the cleaning process becomes even more important. The metallic contaminants on the wafer surface have been a major source of performance failure in IC devices such as increasing the p-n junction leakage, degrading the oxide breakdown voltage, and accelerating the deterioration of carrier lifetime [Kern, 1992]. It has been reported that the metallic contamination on silicon surface needs to be suppressed to less than 1×10^{10} atoms/cm^2 for the manufacture of 64-Mbit DRAM in order to prevent the above failures. In the future, this level should be down to the 1×10^9 atoms/cm^2 [Kern, 1992].

Wet cleaning technique based on H_2O_2 chemistry, proposed first by Kern is still predominantly used in semiconductor device manufacturing for contaminant removal [Kern, 1990], and has been modified in recent years to various methods to improve cleaning effect or reduce chemical consumption [Kern, 1992; Kim et al., 1996]. For example, cleaning solutions using HF/H_2O_2 [Ohmi et al., 1993; Morita et al., 1997], electrolysis-ionized water [Shiramizu et al., 1996], surfactants [Ohmi et al., 1996; Morinaga and Ohmi, 1995], chelating agents [Moninaga et al., 1997] and $HF/HCl/H_2O$ [Ridly et al., 1998] were proposed to increase the cleaning performance on metallic contaminants. Morinaga et al. [1995] reported that an $HF/H_2O_2/H_2O$ solution or dilute HF solution with small amount of surfactant was able to remove Cu effectively. Chung et al. [2000] reported that chelate-added cleaning solution was effective for preventing re-adsorption of metallic contaminants from the contaminated SC-1 ($NH_4OH/H_2O_2/H_2O$) cleaning solution.

In this work, we investigated cleaning solutions based on citric acid (CA) for removing metallic contaminants from silicon surface. Improvement of cleaning performance on metallic contaminants and reduction of chemical costs are expected for the following reasons. CA is common in various plants and has a tendency to form complexes with metal ions. Moreover, CA does not have environmental effects so it is easy to treat wastewater. This paper demonstrates the cleaning ability of CA in removing metallic contaminants from silicon surface.

EXPERIMENTAL

Boron doped Czochralski-grown silicon wafers with a diameter of 200 mm and a resistivity of 9-12 Ω·cm were used in this work. The schematic of the experimental process is shown in Fig. 1. All wafers were pre-cleaned by the modified RCA cleaning. In order to examine the removal efficiency of metallic contaminants on the silicon wafer surface in the cleaning solutions, we intentionally contaminated Fe, Ca, Zn, Na, Al and Cu ions on the wafer surface with the order of 10^{12} atoms/cm^2 by spin coating method [Hourai et al., 1998]. And then the contaminated wafers were cleaned according to the following procedures: 1) overflow rinse with ultra pure water (UPW) for 30 seconds, 2) dip in various cleaning solutions, 3) overflow rinse with UPW for 30 seconds, 4) dry with isopropyl alcohol vapor and N_2 gas blowing. The cleaning solutions used in this work were CA/H_2O, CA/HF/H_2O, CA/HF/H_2O_2/H_2O and CA/NH_4OH/H_2O_2/H_2O mixture. First, the removal efficiency of metallic contaminants was examined by changing the concentration of CA, temperature of cleaning solution and immersion time in CA/H_2O solution. Second, HF or HF/H_2O_2 was added to CA/H_2O solution to

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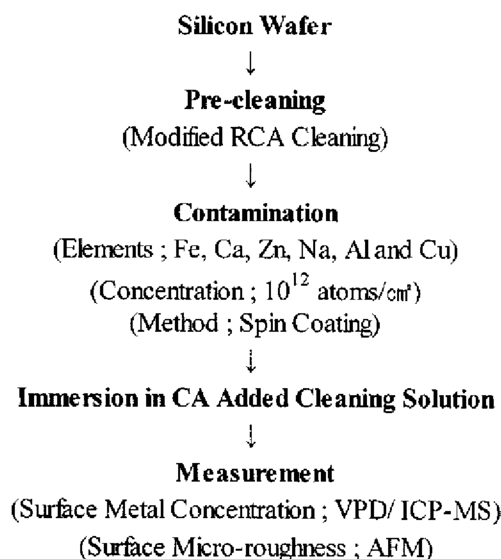

Fig. 1. Experimental process for investigating removal efficiency of metallic contaminants in CA-added cleaning solutions.

Table 1. Chemical composition and process conditions for various cleaning solutions used in experiment

Solution	Composition	Temperature (°C)	Time (min)
Citric acid (A)	0.1-0.8%	25	7
	0.5%	25	3-15
	0.5%	25-80	3
CA/HF	0.5%/X	50	3
	X=50-5,000 ppm		
CA/HF/H_2O_2	0.5%/Y/1%	50	3
	Y=500-5,000 ppm		
HF/H_2O_2	Y'/1%	50	3
	Y'=500-5,000 ppm		
CA/NH_4OH/H_2O_2	0.5%/Z/1%	50	3
	Z=0.3-1%		

increase removal efficiency of Al and Cu. Third, NH_4OH was added to CA/H_2O_2/H_2O solution to examine cleaning ability of CA in alkali solution. Details of these cleaning solutions are summarized in Table 1. The following chemicals used in this work were semiconductor grade: 50% HF, 29% NH_4OH, 30% H_2O_2 and 30% CA. Metal standard solutions (High Purity Standards, 1,000 ppm solution) were used for the intentional contamination.

The concentration of metallic contaminants on the wafer surface before and after cleaning was analyzed by vapor phase decomposition (VPD)/inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer, Elan 6000) [Hall et al., 1996; Kern, 1992]. The detection limits of the metallic contaminants on the wafer surface are 1×10^9 atoms/cm^2 for Zn, Na, Al and Cu and 4×10^9 atoms/cm^2 for Fe and Ca. Wafer surface micro-roughness (root-mean-square roughness) was also analyzed by atomic force microscopy (AFM; PSI, M5) to evaluate the changes of the surface roughness by cleaning solution.

RESULTS AND DISCUSSION

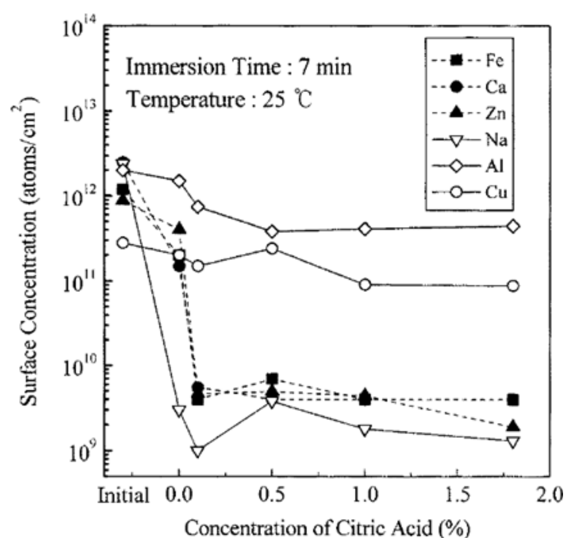

Fig. 2. Removal efficiency of metallic contaminants on the silicon surface as a function of the concentration of CA solution.

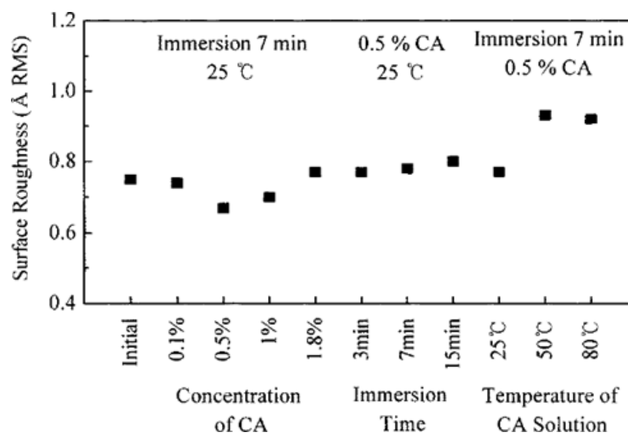

Fig. 3. The changes of micro-roughness of wafer surface treated in each experimental condition.

Fig. 2 shows the removal efficiency of metallic contaminants as a function of the concentration of CA. Immersion time was 7 min and temperature of cleaning solution was 25 °C. In this test, Fe, Ca, Zn and Na were removed to less than 1×10^{10} atoms/cm^2 at all tested CA concentration, while Al and Cu were not removed well. Surface micro-roughness after cleaning was not changed in this concentration range (Fig. 3). Fig. 4 shows the concentration of metallic contaminants on the wafer surface when the immersion time was changed. Fe, Ca, Zn and Na were removed well for short immersion time, while Cu was not removed well regardless of immersion time. Al was slightly removed when wafer was immersed for 15 min. Fig. 5 shows the concentration of metallic contaminants on the wafer surface when the temperature of cleaning solution was changed. The concentration of CA was 0.5% and immersion time was 3 min. Removal efficiency of Al and Cu was increased slightly when the temperature was over 50 °C. But there was no big difference between 50 °C and 80 °C on removal efficiency. The surface was roughened slightly when the temperature was over 50 °C as shown in Fig. 3. It is known that increasing temperature of cleaning solution can affect the rate of reactions or solubility of contami-

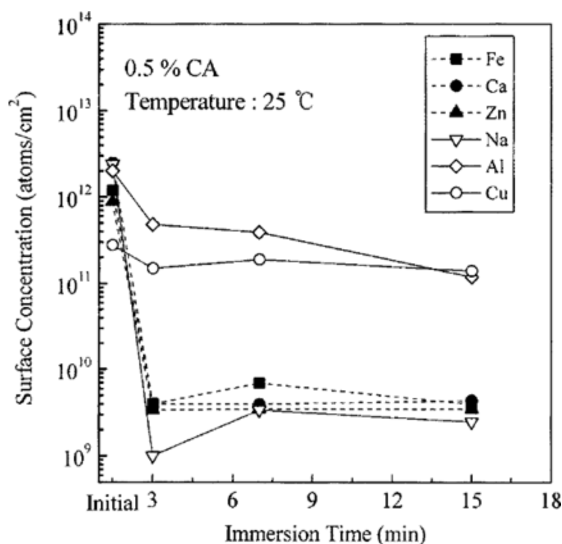

Fig. 4. Effect of immersion time in removing metallic contaminants on the silicon surface.

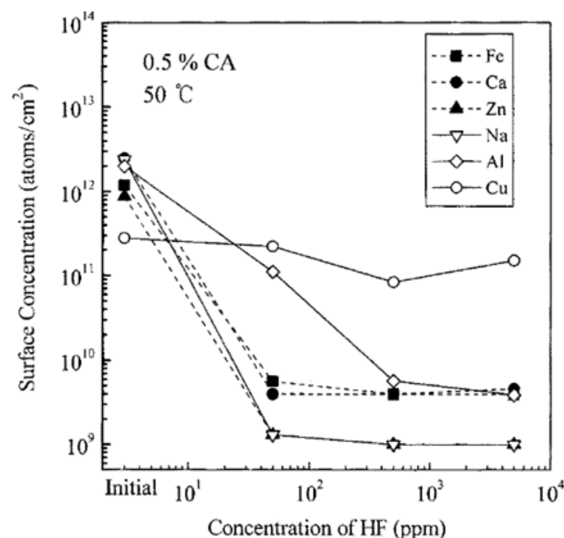

Fig. 6. Removal efficiency of metallic contaminants on the silicon surface as a function of the concentration of HF-added in 0.5% CA solution.

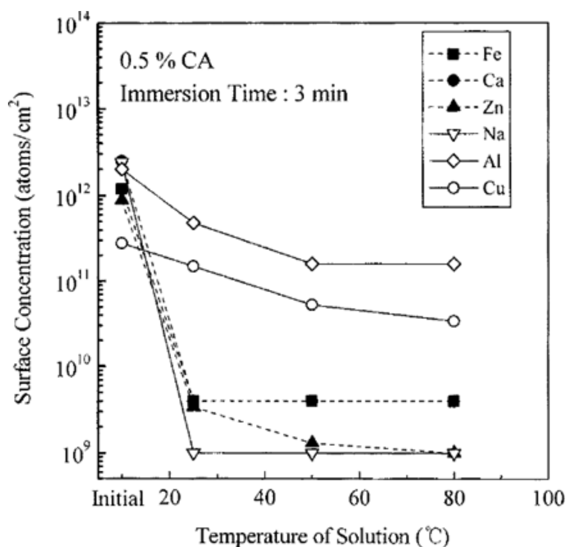

Fig. 5. Effect of temperature of CA solution in removing metallic contaminants on the silicon surface.

nants. Increase of removal efficiency and surface micro-roughness is speculated to be a result of increase of reactivity as temperature increases. Removal of metallic contaminants on the wafer surface is related to chemical bonding between metallic elements and silicon as well as reaction of metal ion and cleaning solution. Therefore, low removal efficiency of Al and Cu in CA solution is considered to be caused mostly by the bonding between metallic contaminants and silicon. As a result, it was found that weak acid, CA, does not have an enough ability to remove Al and Cu from silicon surface, but it is effective to remove Fe, Ca, Zn and Na even at low concentration, low temperature and with short immersion time.

It is known that chemical or native oxides on silicon surface are promptly etched in dilute HF solution and metallic contaminants in oxides are removed at the same time. To increase removal efficiency of Al and Cu, HF was added from 50 ppm to 5,000 ppm to 0.5% CA solution. Temperature of cleaning solutions was 50 °C. Fig. 6 shows the removal efficiency of metallic contaminants in HF added CA solution. Removal efficiency of Al was increased in proportion to the amount of added HF. Al concentration remaining on silicon surface was reduced to the order of 10^9 atoms/cm^2 when HF was added over 500 ppm. However, Cu was not removed well. The difference in the removal efficiency between Al and Cu is thought to be the difference in reactivity with silicon. It is known that Al has a tendency to be included in oxides rather than deposited onto bare silicon surface. On the other hand, Cu is deposited onto bare silicon surface by an oxidation-reduction reaction between Cu ions and silicon [Kern, 1992]. For this reason, Al was removed when the silicon oxide was slightly etched by HF and adsorption of Al was not occurring in CA/HF/H_2O solution without oxidizing agent. But Cu was adsorbed back on the bare silicon surface in HF-added solution.

Fig. 7 shows the removal efficiency of Fe, Ca, Zn, Na, Al and Cu when the contaminated wafers were treated with the CA/HF/H_2O_2/H_2O solution. The concentration of CA and H_2O_2 was 0.5% and 1%, respectively. Temperature of cleaning solutions was 50 °C. When HF was added from 500 ppm to 5,000 ppm to CA/H_2O_2/H_2O solution, all of the tested metallic contaminants were removed very effectively from silicon surface without degradation of surface micro-roughness. It had been reported that Cu contaminant removal efficiency was increased in HF/H_2O_2 solution [Ohmi et al., 1993; Morita et al., 1997]. The same result was obtained in this experiment. The reason why metallic contaminants are removed well in HF/H_2O_2 solution is that metallic contaminants are dissolved in acidic solution and metallic contaminant included in oxides such as Al is also removed by oxide etching. And re-adsorption of Cu is prevented by surface oxidation by H_2O_2. Removal efficiency of Cu, however, was reduced when HF was added more than 500 ppm to CA/H_2O_2/H_2O solution. Similar result had been reported about Cu removal in HF/O_3-UPW cleaning solution [Morita et al., 1997]. In that report, Cu removal efficiency was reduced drastically when HF concentration exceeded 200 ppm. The authors explained this result by sug-

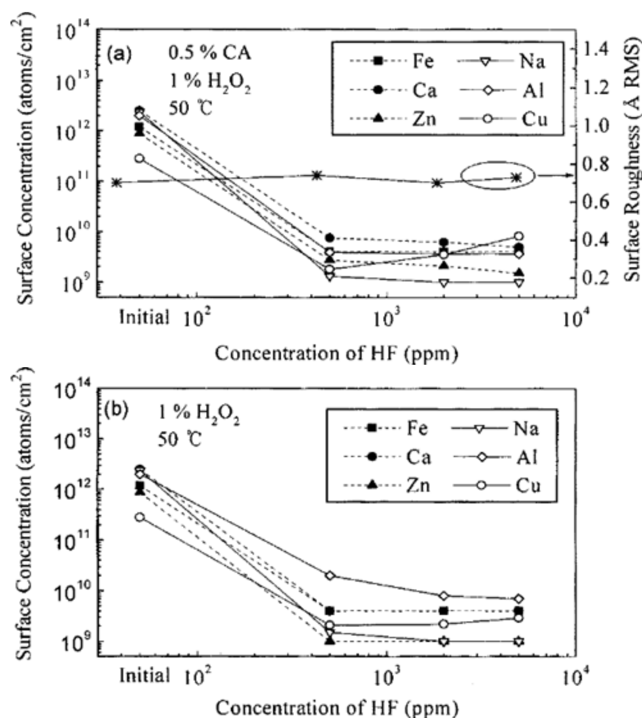

Fig. 7. Removal efficiency of metallic contaminants on the silicon surface as a function of the concentration of HF added in (a) CA(0.5%)/H_2O_2(1%) solution and (b) H_2O_2(1%) solution.

gesting a CuF_2 passivation model that insoluble CuF_2 layer passivated Cu particles on silicon surface when HF was added more than 200 ppm to HF/O_3-UPW solution. And they speculated that the passivated Cu particles could not be removed from the surface by etching of silicon oxide layer. As shown in Fig. 7, Cu concentration remaining after cleaning was less than 1×10^{10} atoms/cm^2 though Cu removal efficiency was reduced with the increase of HF concentration. This is not explained by CuF_2 passivation model mentioned above. So this result was considered by simple oxidation and etching balance model by H_2O_2 and HF. Silicon surface is oxidized by H_2O_2. Cu is almost removed when HF etches oxidized silicon surface. In some stable condition, re-adsorption of removed Cu is prevented by continuous oxidation of silicon surface by oxidizing agent. If the balance of oxidation and etching is disturbed as the concentration of HF is increased, oxide etching exceeds an oxidation of silicon. So Cu can possibly contact and be adsorbed back onto bare silicon surface etched by HF. When the contaminated wafers were treated with the HF/H_2O_2/H_2O solution, the result is also shown in Fig. 7. Metallic contaminants were removed well in HF/H_2O_2/H_2O solution. Therefore, it is thought HF and H_2O_2 in CA/HF/H_2O_2/H_2O solution play a major role to remove metallic contaminants. Though CA/HF/H_2O_2/H_2O solution was very effective in removing metallic contaminants on silicon surface, cleaning effect by CA was not confirmed exactly in CA/HF/H_2O_2/H_2O solution.

Removal efficiency of metallic contaminants is shown in Fig. 8 when NH_4OH was added to CA/H_2O_2/H_2O solution. Temperature of cleaning solutions was 50 °C. Fe, Ca, Zn, Na and Cu were removed less than 1×10^{10} atoms/cm^2 when the concentration of NH_4OH was 0.3% without degradation of surface micro-roughness. Al was not

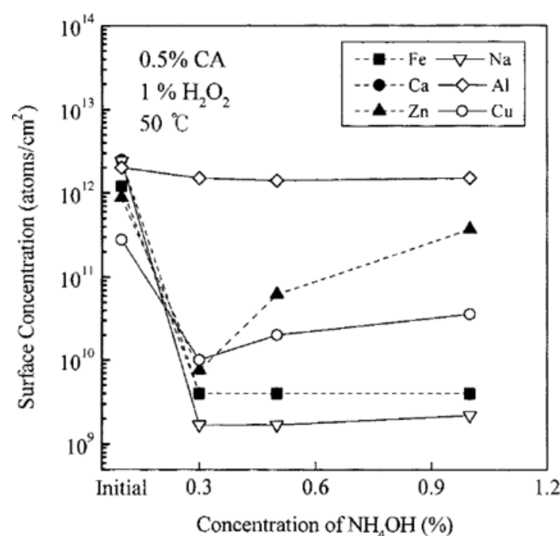

Fig. 8. Removal efficiency of metallic contaminants on the silicon surface as a function of the concentration of NH_4OH added in CA(0.5%)/H_2O_2(1%) solution.

removed regardless of concentration of NH_4OH. NH_4OH/H_2O_2/H_2O is a composition of SC-1 cleaning solution. SC-1 solution is known to be effective in removing organic contaminants or particles on silicon surface, but it has a problem such as metal recontamination. Recently, modified SC-1 solutions with additives have been studied to solve this problem. In this work it has been proved that CA has chelating ability with metals in SC-1 solution. Fe, Ca, Zn, Na and Cu were removed very effectively and prevented from being re-adsorbed in CA/NH_4OH/H_2O_2/H_2O alkali solution. However, removal efficiency of Zn and Cu was decreased as the concentration of NH_4OH was increased. This result is thought to be related to re-adsorption in SC-1 solution. Metal contamination due to SC-1 solution has been studied for many years [Mori et al., 1995; Mouche at al., 1995; Mertens et al., 1998; Loewenstein and Mertens, 1999]. Mori et al. [1995] reported that Zn was adsorbed as metal hydroxide complex in SC-1 solution. Mertens et al. [1998] have found that adsorption of Zn was dependent on the concentration of H_2O_2 and NH_4OH in SC-1 solution. In CA/NH_4OH/H_2O_2/H_2O solution, Zn and Cu can form various complexes with ammine, citrate and hydroxyl ion. Therefore, re-adsorption of Zn and Cu with increase of NH_4OH is considered to be caused by diverse complexing of Zn and Cu in solution. However, the mechanism of re-adsorption of Zn and Cu in CA/NH_4OH/H_2O_2/H_2O solution is not totally understood. In the case of Al, the reason why Al was not removed is thought to be re-adsorption of aluminum hydroxide because Al forms aluminum hydroxide, which is adsorbed easily on silicon surface in SC-1 solution. As a result, it was found that CA was not effective for removing Al and preventing re-adsorption, but CA was very effective in removing Fe, Ca, Zn, Na and Cu in alkali cleaning solution.

CONCLUSION

Cleaning solutions based on CA were investigated for the removal of metallic contaminants on silicon surface. Silicon wafers contaminated with Fe, Ca, Zn, Na, Al and Cu by the order of 10^{12} atoms/cm^2 were treated in various cleaning solutions. First, the concentra-

tion of CA, temperature of CA solution and immersion time in CA/H_2O solution were changed. It was found that acidic CA/H_2O solution is effective for removing Fe, Ca, Zn and Na from the silicon surface even at low concentration, low temperature and with short immersion time.

When HF was added to CA/H_2O solution, Al was removed in proportion to the concentration of HF. But Cu was not removed by the re-adsorption onto bare silicon surface. In $CA/HF/H_2O_2/H_2O$ solution, initial Fe, Ca, Zn, and Na contamination level around 10^{12} atoms/cm^2 was decreased down to the level of 10^9 atoms/cm^2. This result was considered that $CA/HF/H_2O_2/H_2O$ solution has an ability to etch silicon oxide and prevent re-adsorption of metal by generating oxides.

It has been also demonstrated the effect of CA in removing metallic contaminants from silicon surface in alkali solution. Fe, Ca, Zn, Na and Cu contaminated by the order of 10^{12} atoms/cm^2 were reduced down to the order of 10^9 atoms/cm^2 in $CA/NH_4OH/H_2O_2/H_2O$ alkali solution. Therefore, CA could be applicable for improving cleaning effect of metallic contaminants in semiconductor cleaning process when it is used by itself or as additive in SC-1 cleaning solution.

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