

# Different Adsorption Behaviors of Platinum Group Metals on Silicon Surfaces

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The platinum group metals (Pt, Ir, and Ru) with high electronegative value are strong candidate for electrodes of high dielectric films, but the adsorption behaviours and the removal efficiency on Si surface with various chemicals are not clear yet [1].

Fig.1 compares the dependence of metals removal efficiency on various chemicals with high oxidation-reduction potential (ORP) value. The solutions have a good capability to remove metallic impurities such as Cu and Ag, but the amount of Pt and Au residues from Si surfaces does not change so much. Because of these low removal efficiencies of the metals compared to those of light metals, noble metal impurities on wafer surface should be controlled very carefully [2].

Fig.2 represents the adsorption characteristics of noble metal impurities. The contamination level of the metals such as Cu, Ag, and Au is proportional to the contaminants concentration, while the deposited amount of Pt group metals is very low. It is worthwhile to note that the amount of deposition of the group metals is smaller than that of Cu.

Fig.3 shows the dependence of the adsorption behaviours on adding various chemicals to Pt contaminants, where the concentration of added chemicals is fixed at 1 mole/liter. Irrespective of added acidic solutions, the amount of adsorption is not so high. In other words, the NH<sub>4</sub>OH addition in the contaminants increases the amount of deposition on the silicon surface. Fig.4 shows the influence of NH<sub>4</sub>OH concentration in Pt solution upon the amount of Pt impurities on silicon surface, where the amount increases with the increase of the concentration.

Fig.5 compares the concentration of Pt containing solutions after filtrating through two ion exchange resins. The result at the pH value of 7 or below shows that the concentration has a big difference *before and after* filtrating through an anionic ion exchange resin, but it is almost same in case of a cationic ion exchange resin. Moreover, at pH value of 10, the filtrated concentration using anion exchange resin is higher than those of above two solutions, but the concentration through cation ion exchange resin is relatively much decreased. Judging from relationship between the amount of Pt deposition in solutions and the concentration difference after the filtration as stated above, the metallic Pt in solution with pH value of 7 or below has negative charge, whereas its charge on increasing the pH value by adding NH<sub>4</sub>OH seems to change from negative to positive.

The authors point out that the deposited amount of the noble metals on wafer surfaces strongly depends on their charge states (positive, negative or neutral) as well as their electronegative values and oxide formation energies.

## References

- [1] Geun-Min Choi, Francesco Pipia, and Tadahiro Ohmi, Extended Abst. of the Int'l Conf. on SSDM, pp.174, Sendai, October (2000).  
[2] H. Morinaga, M. Suyama, and T. Ohmi, J. Electrochem. Soc., **141**, 2834 (1994).

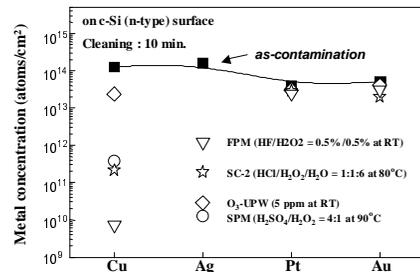


Fig.1 Removal efficiencies of noble metals on c-Si surface with cleanings.

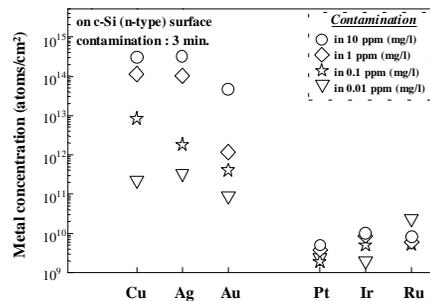
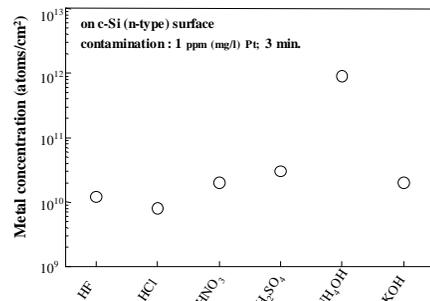


Fig.2 The amount of adsorptions on c-Si surfaces with varying concentration of contaminants.



Added 1 mole/liter chemicals to 1 ppm (mg/l) Pt solution

Fig.3 Dependence of Pt adsorption on c-Si surfaces with added chemicals.

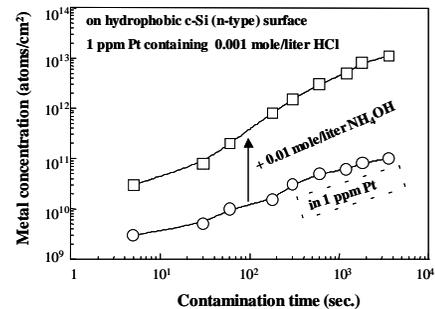


Fig.4 The amount of Pt impurity on Si surface as a function of increasing dipping time.

Filtration of contaminants containing Platinum (Pt)	Pt concentration (ppm: mg/liter)		
	pH 2	pH 7	pH 10
<i>Before filtrating</i>	1.00	0.97	1.30
Anion ion exchange Filtrating (R(NR <sub>2</sub> ) <sub>2</sub> (OH) <sub>2</sub> )	0.01	0.01	0.07
Cation ion exchange Filtrating (R(SO <sub>3</sub> ) <sub>2</sub> (H) <sub>2</sub> )	0.95	0.92	1.09

Fig.5 Ionic states of Pt impurity with varying pH values in contaminants.