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Outgas-Free, Corrosion-Free Metal Surfaces for ULSI Manufacturing

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Realization of an ultra-clean process environment, in which contamination from molecules adsorbed by the wafer surface is fully controlled, is extremely important for the production of future submicron ULSI devices.

The key to the achievement of such an ultra-clean process environment is the proper treatment of the surface of the stainless steel. That is extensively used in the ultra-high purity gas supply line and the process chamber. Of central importance is controlling the process ambience for minimized both outgas and corrosion-related contamination.

1. Introduction

Efficient submicron production ULSI of can not be achieved without maximum control of contamination. In addition to eliminating solid dust, organic materials, heavy metals and native oxide films in the process ambience, it is important to limit also that impurity molecules, mainly of H_2O, adsorbed by the wafer surface. In order to eliminate the emission of dust and gas from the manufacturing equipment itself, there should be a self-cleaning capacity in order to regularly remove material generated by the process itself and sticking to the inner surface of the equipment. For this purpose it is essential for the gas-contacting surface of the gas delivery, the inner surface of the process chamber and the exhaust line be sufficiently resistant to the corrosion by etching gases, the purpose of this paper is to report on the result of a study oxygen passivation or fluorine passivation treatment using a dry ambient. The passivation treatment is applied to the surface mirror-polished stainless steel which is extensively used in the gas supply line and the process chamber for ULSI manufacturing. The resultant outgas performance and anti-corrosiveness of the treated surfaces are reported.

2. Experimental

Usually stainless steel 316L, extensively used as a material for the gas supply system and the process chamber for ULSI manufacturing, undergoes electro-polissing or electro-chemical buffing. This brings its surface to a mirror finish, free of a fragmented layer[1]. It is then immersed in a nitric acid solution of about 60 ^{o}C to form a very thin passivated film over surface. As this method of passivated film formation is a wet treatment, there remains large quantities of moisture and solution within the film and on the boundary between the stainless steel surface and the film. The impurities, mainly consisting of this residual moisture, diffused into the steel and subsequently contaminate the process ambience.

At the same time, the stainless steel surface that has been passivated by the wet treatment lacks resistance to corrosion by

chlorine- or fluorine-based etching gases.

We carried out an experiment in which the formation of a passive film was achieved by, instead of the wet treatment with nitric acid solution, treatment with oxygen gas and fluorine gas in a process gas ambient with moisture of 10 ppb or less. The sample for oxygen-passivation[2], used in an outgassing test, were electropolished SUS 316L pipes of 3/8" in bore and 2 m in length. Those used in a corrosion-resistance test with a 35% solution of hydrochloric acid, were SUS 316L plates having undergone electrolytic compound polishing. The temperature for this passivation process ranged from 300 ^{o}C to 500 ^{o}C. In the outgassing test, evaluation and analysis were conducted by atmospheric pressure ionization spectrometry (APIMS)[3]. Ar gas with 2 ppb or less of moisture through sample piping at a rate of 1.2 ml/min. The total quantity of the effluent gas from the piping end, which was to be assessed, was fed to the APIMS unit. Fig.1 illustrates the experimental system.

In the corrosion-resistance test, the samples were immersed in a 35% hydrochloric acid solution. The elapsed time before the generation of hydrogen gas by corrosion was measured.

For fluorine-passivation[4], electro-polished SUS 316L samples were stripped of a naturally oxidized film formed over their surface. This was accomplished with a 0.5% aqueous solution of HF, followed by baking in a reaction vessel, whose inside was then to let in high-purity fluorine (with less than 1 ppm each of O_2 and HF) from a fluorine generator.

Direct fluoridation was carried out for 80minutes under 1 atm and at 220 ^{o}C. After that, the products were thermally modified by heat treatment for 1 hour at 320 ^{o}C in a high-purity N_2 gas ambience under 1 atm. The composition, outgassing performance and corrosion-resistance of the resultant fluorine-passive films were respectively determined by X-ray photoelectron spectroscopy (XPS), APIMS and exposure to wet diluted HF gas (with $HF:H_2O:N_2$ ratio equal 5:1:94).

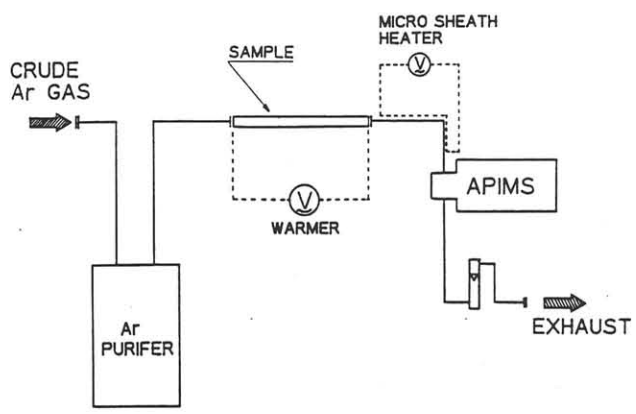

Fig.1 Schematic diagram of measurement system to evaluate outgassing from tubes. Tube sample is baked with warmer (4).

3. Result and Discussions

Fig.2 shows comparative date on the outgassing characteristics of SUS 316L-EP passivated pipes. Passive films were formed by thermal oxidation with oxygen gas in a high-purity dry ambience with moisture of 10 ppb or less and by using other SUS 316L-EP pipes whose passive film was conventionally formed (using nitric acid solution). While the latter continued to generate about 50 ppb

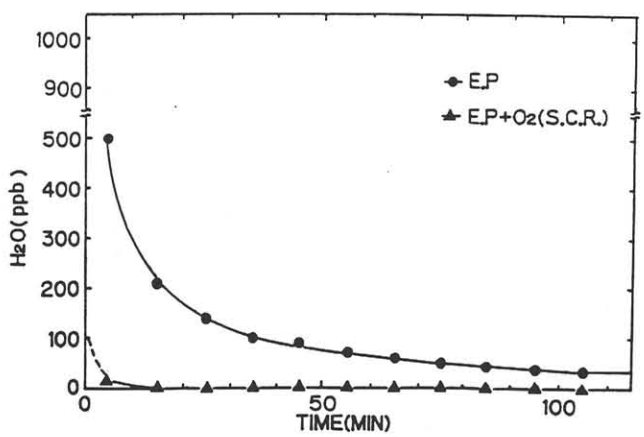

Fig.2 Time dependence of water concentration in argon gas passed through sample tubes at 25 ^{o}C. (stainless steel 316L-EP O_2 passivation)

of moisture even after two hours, the moisture from the former become equal to the background level within 15 minutes[2]. Table 1 shows the results of the corrosion-resistance test in which SUS 316L-EP plates, over which a passive film had been formed by thermal oxidation in a temperature range of 300 °C to 500 °C, were immersed in a 35% solution of hydrochloric acid. A sample which underwent thermal oxidation for nine hours at 450 °C took 45 minutes to generate corrosion-deriving hydrogen gas. This indicated greater corrosion-resistance than other samples.

Next, with respect to the characteristics of the fluorine-passive film formed, Fig.3 shows the results of determination by XPS of the composition of the film after thermal modification. Whereas the main fluoride was FeF_2, the out-ermost layer of the film consisted of CrF_2.

Fig.4 shows the outgassing characteristics of SUS 316L-EP pipes over which a passive film was conventionally formed by using a nitric acid solution. It is seen that there is an improvement in outgassing characteristics as well over the conventional way of passivation. Fig.5 shows the results of exposure of samples to diluted HF gas for 14 days[4]. While the electropolished SUS 316L were intensely corroded, those with a fluorine-passive film were found completely free from corrosion.

Table 1 Corrosion-resistance of O_2 passivation film in 35% HCl solution.

Sample	Film thickess (A)	Result
non-oxidized	7	Gas generated immediately after dipping
300℃, 4hr	110	Interference color-gold discolored immediately after dipping, gas generated after about 20 minutes
400℃, 4hr	126	The result is as same as above
450℃, 4hr	140	The result is as same as above
450℃, 9hr	164	Gas generated after about 45 minutes
500℃, 4hr	180	Gas generated after about 30 minutes

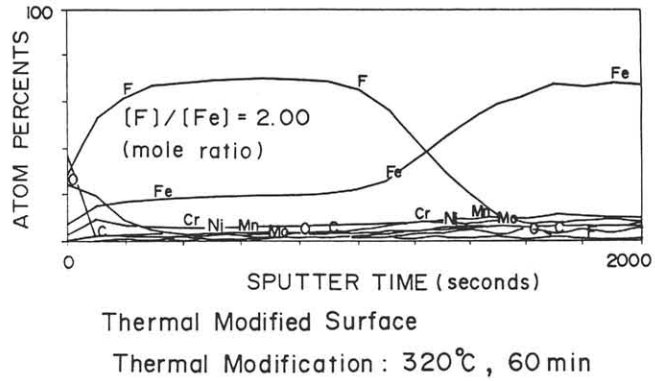

Fig.3 Depth profile of XPS spectra from the thermal modified 316L stainless steel surface.

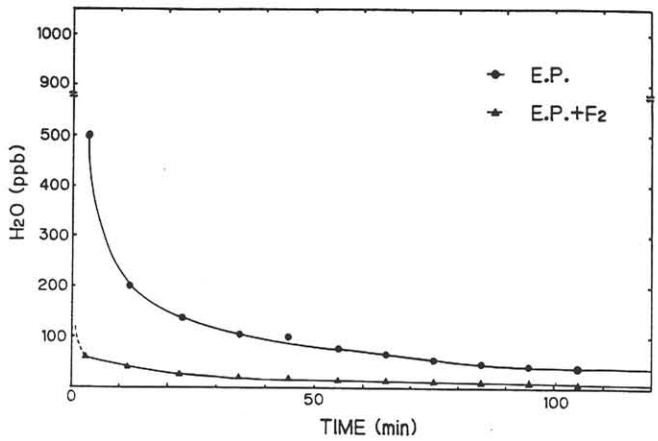

Fig.4 Time dependence of water concentration in argon gas passed through the sample tubes at 25 °C. (stainless steel 316L-EP F_2 passivation)

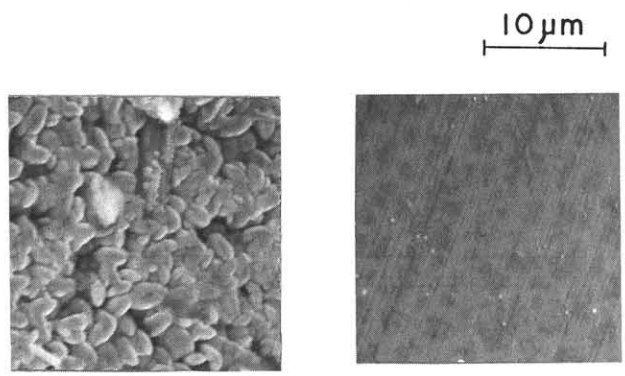

Fig.5 SEM photographs of the fluorine passivated and the unpassivated 316L stainless steel surfaces exposed to the wet HF gas.
wet HF gas : HF 5%, H_2O 1%, N_2 94%

4. Conclusions

It has been revealed that the passivation of stainless steel having no mirror-polished process-degenerated layer by thermal oxidation or fluoridation yield gives an outgas-free and corrosion-free metal surface.

Formation of a passive film by thermal oxidation, in particular, was found to reduce the residual moisture in the film and on the boundary between the stainless steel surface and the film. This eliminates contamination by outgassing, mainly moisture, and results in remarkable resistance to corrosion by chlorine-based etching gas.

These results indicate that the materials for the gas supply line, an essential factor to the control of process ambients, can be further improved in performance. Also, the formation of a corrosion-free metal surface on the internal surface of the process chamber makes possible the cleaning of by-products of the reactions from the chamber walls, without having to actually open the chamber. A system with such a self-cleaning function could play a decisive role in improving the utilization automation of the ULSI production line.

5. Acknowledgment

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6. References

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