Al_2O_3 Passivation Film on Austenitic Stainless Steel Free From Plasma Damage

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It is reported that Cr_2O_3 film on stainless steel has an excellent corrosion resistance for halogen gases [1]. However, in the case of ozonized gas having strong oxidizability, Cr_2O_3 (Cr^{3+}) film is oxidized and CrO_3 (Cr^{6+}) is generated. CrO_3 has low vapor pressure, and passivation film has disappeared. Al_2O_3 passivation film on austenitic stainless steel that we developed shows good corrosion resistance for ozonized gas, corrosive halogen gases and Cl, F radicals.

Al_2O_3 passivation film has been formed on austenitic stainless steel containing 4-wt % Al by selective oxidation of Al in a H_2/H_2O environment. The oxidation of Al is given by the following equation in H_2/H_2O environment. Fe and Cr are also shown by the similar equation.

$$2Al + 3H_2O = Al_2O_3 + 3H_2 \qquad (1)$$

While, the oxygen potential is related to pH_2/pH_2O ratio as follows:

$$2H_2 + O_2 = 2H_2O: \qquad (2)$$

$$\Delta G^\circ = -RT \ln\left(p_{H_2O}{}^2 \big/ p_{H_2}{}^2 p_{O_2} \right) \qquad (3)$$

$$RT \ln p_{O_2} = \Delta G^\circ - RT \ln\left(p_{H_2}{}^2 \big/ p_{H_2O}{}^2 \right) \qquad (4)$$

From this equation, the stable state of each element is decided by the magnitude correlation of oxygen potential between various oxide and H_2/H_2O mixing gas at the fixed temperature. In the environment with $pH_2/pH_2O \geqq 1x10^4$ at 900℃, oxygen potential of Al_2O_3 is lower than oxygen potential of H_2/H_2O mixing gas. So, Al is oxidized to Al_2O_3 by H_2O. While, oxygen potential of Cr, Fe and Ni oxide is larger than H_2/H_2O mixing gas, each oxides are resolved and discharge oxygen in order to keep equilibrium. Al and O are detected up to 70nm showing that Al_2O_3 film is formed by these oxidation procedures (Fig.1). From the binding energy of XPS spectrum (not shown), the chemical states of Fe, Cr and Ni are confirmed as metallic rather than oxidized ions indicating that oxide is etched off by H radical or reduced by Al in some regions of the surface.

Al_2O_3 film has good corrosion resistance for ozone gas having the strong oxidizability (10% O_3 gas balanced O_2 gas) and halogen gases (Cl_2 and so on). Al_2O_3 film gets no damage for O_3 gas. Because Al is typical elements and the phase does not change. Moreover, Al_2O_3 is very stable thermodynamically. So it is considered that Al_2O_3 film is given no damage.

Al_2O_3 passivated surface has an excellent resistance performance in the plasma environment. We have experimented in the range of plasma potential below 50 V. In the range of plasma potential below 50 V in the Cl_2 plasma (flow rate ratio:Ar/Cl_2 = 9/1, 20mTorr, 1 h) it is found that Al_2O_3 film has no surface damage by Cl radical from observing SEM image (Fig.4). From XPS measurement, Cl was detected for SUS316L electro-polish (EP) surface in the depth direction. However, on Al_2O_3 passivated surface, Cl was not detected (Fig.2). This result confirms that corrosion was not observed on the stable Al_2O_3 surface when it is exposed to extremely Cl radical. While, in the case of Ar/NF_3 = 9/1 at 20mTorr ambient for 1 h, Al_2O_3 film is substituted to AlF_3 over 30 nm from the surface although the plasma potential is only 10V (Fig.3). However, no damage on the passivation film is found from SEM observation (Fig.4), because AlF_3 that is generated is very stable material as well as Al_2O_3 thermodynamically. So it is considered this passivation film has a good performance for plasma environment including F radical.

We have established the selective oxidation technology of the alloy. Al_2O_3 passivation film on austenitic stainless steel has an excellent resistance and it is usable as a peripheral material of the semiconductor manufacturing equipment.

References

[1] Y. Shirai, M. Narazaki and T.Ohmi, IEICE Trans. Electron., Vol.E79-C, No.3, March 1996.

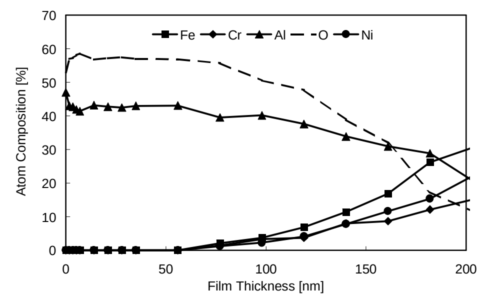


Fig.1 XPS spectra of Al_2O_3 passivated austenitic stainless steel surface.

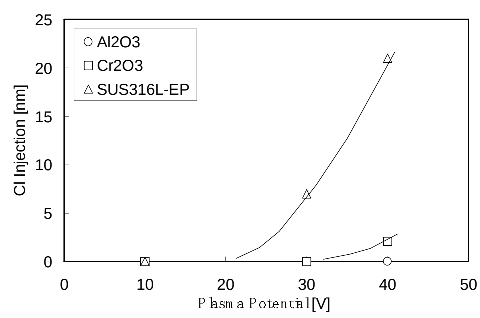


Fig.2 Amount of Cl injection into the depth direction after Cl_2 plasma irradiation (flow rate ratio:Ar/Cl_2 = 9/1, 20mTorr, 1 h).

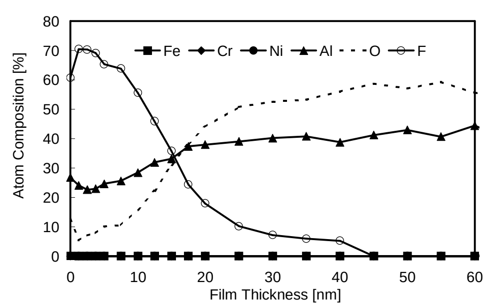
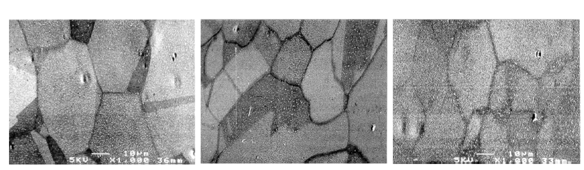


Fig.3 XPS spectra of Al_2O_3 passivated austenitic stainless steel surface after NF_3 plasma irradiation (flow rate ratio:Ar/NF_3 = 9/1, 20mTorr, 1 h, plasma potential:20V).



Initial Ar/Cl_2 Ar/NF_3

Fig.4 SEM images of Al_2O_3 passivated austenitic stainless steel surface after plasma irradiation.