Decontamination of Co, Mo in SF_6/O_2 RF Plasma

Byung-Ju Lim, a Sang-Pil Yun, a Yong-Soo Kim, a Jong-Heon Jeong b, Won-Jin Oh b
a Department of Nuclear Engineering, The Hanyang Univ.
b KAERI (Korea Atomic Energy Research Institute)

1. Introduction

Metal surface processing using for plasma has been highlighted in nuclear industry because the dry decontamination method has been strongly recommended, satisfying the requirement of drastic secondary waste reduction while maintaining the same level of efficiency with current wet decontamination method. Important reaction of plasma decontamination is a fluorination between metal surface and fluorine gas and reactants from fluorination are volatile compounds which have very low melting temperature. DC bias or adding to inert gas (He, Ar, N2) with fluorination can highly increase reaction rate.

In this paper, we experimented on SF_6/O_2 reaction rate with Mo, Co metal and compared with CF_4/O_2 results. It appears that SF_6/O_2 is more efficient than CF_4/O_2 about 2 times in etching rate (um/min).

2. Methods and Results

Plasma reactor is a diode type and r.f. (13.56 MHz) power up to 600 W can be applied between the parallel electrodes. The distance between them remains 10 cm during the current experiments. Sample can be heated up to 1200°C electrical heater inside the reaction chamber. Mass flow controller can control finely and flow rate remains 50sccm. Total gas pressure inside chamber is maintained at around 0.45 Torr during experiments.

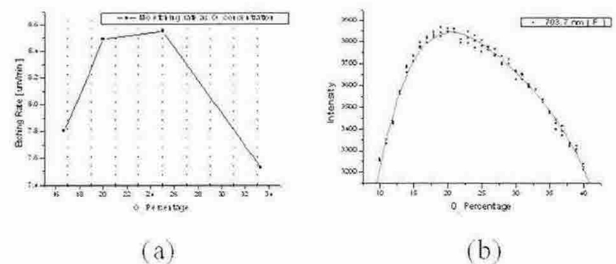
2.1 Specimen Preparation

Non-radioactive metal samples (Co, Mo) with 99.8% purity are used as specimens. We manufactured a thin disk type in 0.7mm thickness from cylinder type which has separately 10mm and 5mm radius using for low-speed diamond cutter. Prior to the sample loading, the surfaces of the specimens are polished as mirror-like by grit 1200 sand paper, cleaned by ultrasonic cleaner and baked at 2oo°C for 10 minutes in a vacuum to evaporate the absorbed moisture on the surface.

2.2 Experimental Procedure

We remained as 220 W in RF power, 0.45 Torr in pressure, and thirty minutes in reaction time at all experiments. First of all, Mo etching rate is measured to find the most efficient reaction of SF_6/O_2 plasma under changing O_2 ratio. In the most efficient O_2 ratio, etching rate of each specimen is measured as temperature. Etching rate is determined by weight loss measurement before and after the reaction with an electro-micro balance (BP210D, Satorius) whose sensitivity limit is 10^{-5}g. Weight loss is expressed in um/min. OES (Optical Emission Spectroscopy) analysis is accompanied with the main experiments to diagnose and determine the plasma parameters and thus to understand the reaction mechanism.

Figure 1 shows that the most efficient O_2 rate of SF_6/O_2 plasma is about 25 %. Result that fluorine quantity is the maximum from OES analysis when O_2 rate is 20 % appears that essential reaction of the surface is fluorination reaction.



(a) (b)

Figure 1. (a) Etching rate of Mo as O_2 percentage at 260 °C SF_6/O_2 plasma (b) OES analysis about RF plasma as O_2 percentage

2.3 Results of Metallic Molybdenum reaction

Etching rate is measured as temperature using SF_6/O_2 and CF_4/O_2 gas in 20% O_2 ratio and increase as temperature. We can know that SF_6/O_2 plasma is more reactive than CF_4/O_2 about 2.5 times at Mo reaction.(Figure 2.)

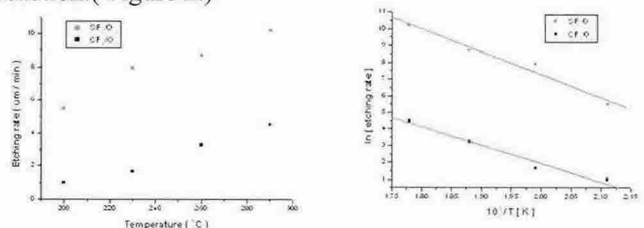
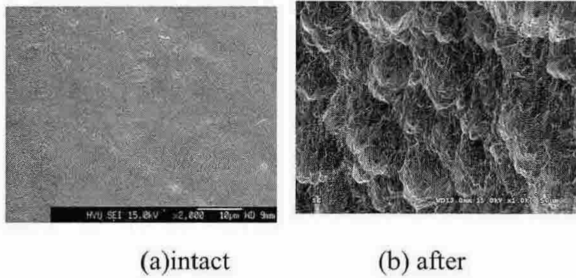


Figure 2. (a) Etching rate of Mo as temperature at SF_6/O_2 plasma and CF_4/O_2 (b) Arrhenius plot

Reaction speed is expressed by basic thermodynamic equation k = a exp $(-E_a/RT)$, k is reaction rate, E_a is activation energy. Plot shape is appeared linearly by changing results with Arrhenius plot. Activation energy of SF_6/O_2 is 14.932 KJ/mol, that of CF_4/O_2 is 39.334 KJ/mol.

In Results of SEM analysis before and after, we can confirm the intensive reaction of surface (Figure 3)

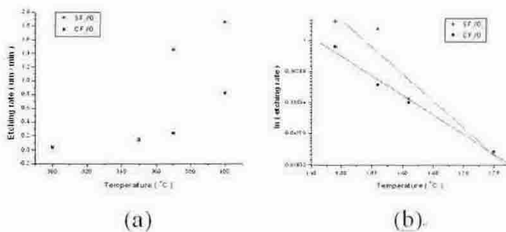


(a)intact (b) after

Figure 3. SEM analysis of Mo before and after the reaction at 290 °C SF_6/O_2 plasma (X 10K)

2.4 Results of Metallic cobalt reaction

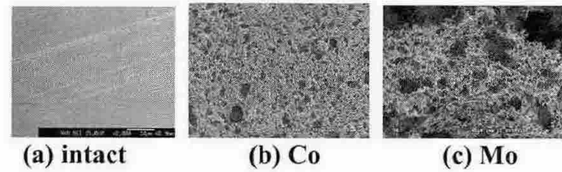
When using for Both CF_4/O_2 and SF_6/O_2 gas, etching rate of Co metal is very low (< 0.03 *u*m/min) below 350 °C temperature. Above 350 °C, it increases as temperature and SF_6/O_2 plasma is more reactive than CF_4/O_2 about 2.5 times in Co reaction. From Arrhenius plot, activation energy of CF_4/O_2 is 105 KJ/mol, that of SF_6/O_2 is 144.8 KJ/mol.(Figure 4.)



(a) (b)

Figure 4. (a) Etching rate of Co as temperature at SF_6/O_2 plasma and CF_4/O_2 (b) Arrhenius plot

We can know that metal surface get rougher after the reaction, and surface reaction of SF_6/O_2 gas is more intensive than that of CF_4/O_2 from SEM analysis at 400 °C. (Figure 5.)



(a) intact **(b) Co** **(c) Mo**

Figure 5. SEM analysis of Co before and after the reaction at 400 °C SF_6/O_2 plasma (X 10K)

3. Conclusion

We experimented on the etching rate of Metal Mo and Co surfaces using for SF_6/O_2 RF plasma and compared with CF_4/O_2 results. Reaction is the most efficient in 25 % O_2 percentage. Under the same conditions, SF_6/O_2 gas is more reactive than CF_4/O_2 gag about 2~2.5 times. Result that fluorine quantity is the maximum from OES analysis when O_2 rate is 20 % appears that essential reaction of the surface is fluorination reaction.

If induced DC bias voltage or added inert gas, we will gain etching rate higher than current results

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