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UO_2 Etching by Fluorine Containing Gas Plasma

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Abstract

Research on the dry etching of UO_2 by using fluorine containing gas plasma is carried out for DUPIC (Direct Use of spent PWR fuel In CANDU) process which is taken into consideration for potential future fuel cycle in Korea. CF_4/O_2 gas mixture is chosen for the reactant gas and the etching rates of UO_2 by the gas plasma are investigated as functions of substrate temperature, plasma gas pressure, CF_4/O_2 ratio, and plasma power. It is tentatively found that the etching rate can reach 1000 monolayers/min. and the optimum CF_4/O_2 ratio is around 4:1.

I. Introduction

According to the future nuclear power program, the number of CANDU reactors to that of PWRs reaches one third in Korea in early 21st century, which coincidentally makes the idea of DUPIC fuel cycle plausible. The idea basically stems from that the fissile isotope inventory in discharged PWR spent fuels (~1.6w/o) is more than that in the natural uranium (~0.7w/o) which is used for CANDU reactor fuel. Feasibility study (phase I) of the idea has been completed and it is in second phase now. In DUPIC process first step is to separate the burned UO_2 fuel from the disassembled PWR spent fuel rods. The extracted spent UO_2 fuel is 'oxidized and reduced' repeatedly, according to so-called OREOX (Oxidation and REduction of OXide fuel) process, to be made for resinterable powder. Along with the main process UO_2 residuals on the decladded hull should be removed in conformity with a requirement or a criteria that the transuranic (TRU) recovery in the overall decladding process must be greater than 99.9%. Most candidate mechanical decladding technologies are unable to recover more than 98 to 99.5% of the heavy metal/metal oxide. Therefore,

another process for further decontamination of the cladding is required. For the secondary process a dry etching technique by fluorine containing gas plasma is being studied since the whole DUPIC fuel manufacturing processes are supposed to be dry ones and the high reactivity of uranium compound with fluorine is well-known. For current study only CF_4/O_2 mixture gas plasma is used.

II. Brief Review on Related Earlier Works

Low temperature (below 800K) reaction of UO_2 under one atmospheric pressure of F_2 was studied by weight loss measurements by Iwasaki [1] and by Vandenbussche [2]. Under these conditions ultimate reaction products are UF_6 and O_2 while a variety of intermediate reaction products such as $(UO_2)_4F$ and UO_2F_2 are identified. Contrary to these studies a quasi-equilibrium reaction model predicted that at high temperature (above 1000K) under low pressure of F_2 (10^{-7} ~ 10^{-4} Torr) the higher fluoride UF_5 and UF_6 formations should be suppressed in favor of UF_4 formation and atomic fluorine [3,4]. However, in those studies elucidation of the reaction mechanism was limited since they were overall reactions in equilibrium or in quasi-equilibrium.

Machiels and Olander performed kinetic study on $UO_2 + F_2$ reaction by modulated molecular beam mass spectrometry in 1977 and found that the reaction product is UF_4 and the reaction probability is higher than 10^{-2} (Figure 1). They claimed that the reaction mechanism is the second order surface reaction coupled with double diffusion process [5]. Their results, however, should be carefully extrapolated to those of the reactions under high pressure and low temperature since their experiment was carried out at high temperature above 1000 K under high vacuum condition.

One of the most popular gas mixture used for plasma etching in the semi-conductor industry is CF_4/O_2 mixture gas. Consequently a number of studies on the mixture gas plasma reaction have been carried out. It is relatively well-known that major radicals produced during the plasma generation are CO, CO_2, COF_2, F_2 and F though the mole fractions of the products depend on the O_2 content in the feed gas. CF_4/O_2 mixture gas plasma reaction paths and the major product species are schematically shown in Figure 2 [6]. However, it is always comprehended that the produced radicals and their mole fractions are strongly influenced by plasma configuration such as plasma power, gas pressure, distance between electrodes, etc.

Recently Martz examined the etching of Pu and PuO_2 by same mixture gas plasma [7]. He found that the etching rate of Pu metal is a few Ås/sec while that of PuO_2 is about five to ten times greater. In his experiment O_2 mole fraction was set to be 10% and total pressure was varied from 0.1 Torr to 0.6 Torr. His reaction chamber is a long cylinder made of thick quartz and the r. f. power of 50W was applied by wound electrical coil outside.

III. Experimentals

The apparatus for UO_2 etching by CF_4/O_2 mixture gas plasma was designed and manufactured to meet the experimental purpose. Schematic diagram of the apparatus is shown in Figure 3. In the reaction chamber sample substrate can be heated up to 800°C by electrical heater and maximum 4" diameter disk or wafer-like sample can be etched with up to r. f. power of 600W. The mass flow controllers fine-control the gas flows rate up to 100 sccm. Distance between the parallel electrodes can be adjusted up to 10cm.

In the experiments thin disk of natural uranium dioxide is used for samples which is cut out of pellet. Prior to the etching reaction it is polished by grit 600 sandpaper, cleaned by ultrasonic cleaner and baked at 200 °C for 10 minutes. Sample weight is measured by electro-micro balance before and after the sample etching in the reaction chamber. The chamber pressure is maintained at 0.3 Torr while O_2 mole fraction is varied. The distance between the parallel electrodes is stationary for current experiments.

IV. Results and Discussion

First, the etching rate at 200 °C substrate temperature was examined with various CF_4 / O_2 ratios, 6:4, 7:3, 8:2, and 9:1. Exposure duration was 100 minutes and r. f. power of 50W was supplied. Experiments were repeated with higher r. f. power, 100W and 150W, to see the rate enhancement. The etching rate is estimated with following formula:

$$\frac{(N_a / M)}{(N_a \rho / M)^{2/3}} \frac{w}{At} \quad \text{(monolayers/min)}$$

where M = UO_2 atomic mass, 270.03 g/mole

ρ = UO_2 density, 10.96 g/cm^3

A = area of UO_2 sample

w = weight loss due to the etching

t = exposure duration to plasmas.

The results are plotted in Figure 4.

The whole experiments were repeated at 300 ^{o}C substrate temperature and the results are shown in Figure 5.

From Figure 4 and 5 it is tentatively found that optimum CF_4 / O_2 ratio is around 4:1 at all temperatures and the etching rate at the gas composition reaches around 1000 monolayers/min. which is twice larger than those at other compositions. With increased temperature at 300 ^{o}C the rate remains almost same with those at 200 ^{o}C and the peak at optimum gas composition is diminishing. The etching rate is linearly proportional to r. f. power while it is insensitive to gas compositions at 50W r. f. power.

The etching rate in this experiment is about ten times higher than that for PuO_2 etching, however, the optimum gas compositions are similar in both cases [7]. It is fundamentally believed that fluorine atoms or fluorine containing radicals reacts with surface atoms, either Pu or U atom, and the carbon residuals on the surface decomposed from carbon tetrafluoride during the reaction may retard the reaction. This is the reason that oxygen gas is contained in the feed gas to pick up the carbon atoms to form volatile species such CO or CO_2. Also in this experiments, the etching reaction except at the optimum gas composition seems to be suppressed in a similar way.

The overall reaction in this study is believed to produce uranium tetra- or hexafluorides and carbon mono- or dioxide, or all together. They will be identified by using quadrupole mass spectrometer and the study on the UO_2 stoichiometry change and surface modification will be followed. In addition the reaction will be examined as a function of mixture gas pressure to derive reaction mechanism.

References

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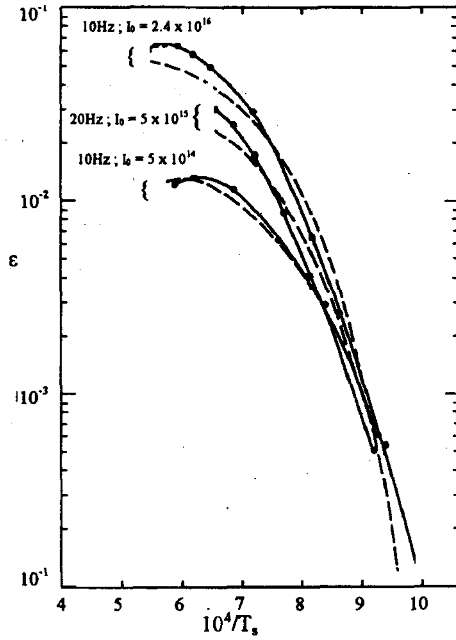

Figure 1. Reaction probability of UF_4 by UO_2 + F_2 gas[1]

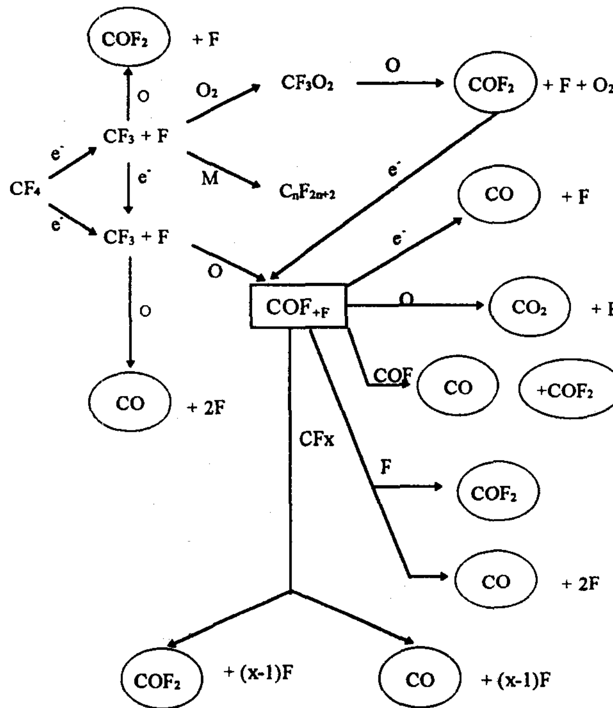

Figure 2. CF_4 + O_2 mixture gas plasma reaction

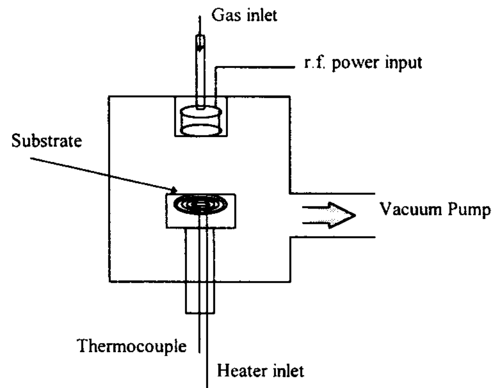

Figure 3. Schematic of Plasma Etching Apparatus

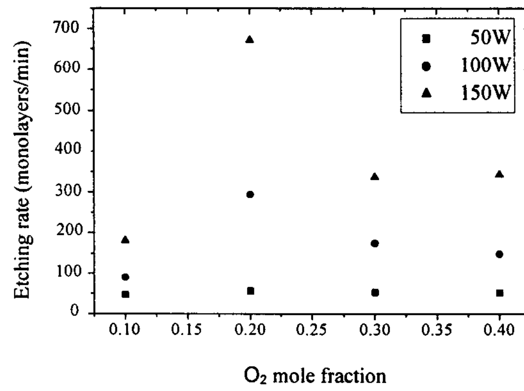

Figure 4. Etching rate v.s. O_2 mole fraction at 200^oC
(flow rate : 50sccm, reaction time : 100min.)

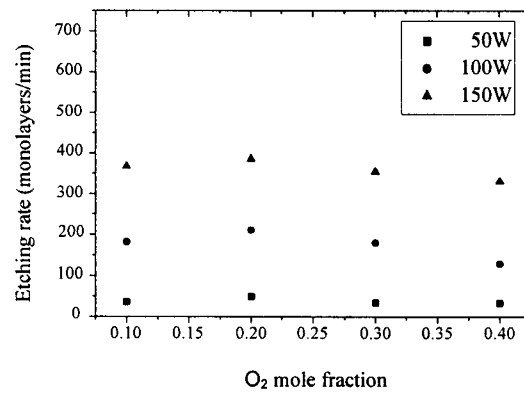

Figure 5. Etching rate v.s. O_2 mole fraction at 300^oC
(flow rate : 50sccm, reaction time : 100min.)