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Etching Reaction of UO_2 with CF_4/O_2 Mixture Gas Plasma

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Abstract

Research on the etching reaction of UO_2 with CF_4/O_2 gas mixture plasma is carried out. The reaction rates are investigated as a function of CF_4/O_2 ratio, plasma power, and substrate temperature. It is found that there exists an optimum CF_4/O_2 ratio around 4:1 at all temperatures up to 370℃ and surface analysis using XPS (X-ray Photoelectron Spectroscopy) confirms the result. Peak rate at the optimum gas composition increases with increasing temperature. Highest rate obtained in this study reaches 1050 monolayers/min. at 370℃ under r. f. power of 150 W, which is equivalent to about 0.5μm/min. The rate also increases with increasing r. f. power, thus, higher power and higher substrate temperature will undoubtedly raise the etching reaction rate much further. This reaction seems to be an activated process, whose activation energy will be derived in the following experiments.

Key Words : uranium dioxide, etching, plasma, CF_4/O_2 gas, dupic

1. Introduction

According to the future nuclear power program in Korea, the number of CANDU reactors to that of PWRs reaches one third in early 21st century, which coincidentally makes the idea of DUPIC (Direct Use of PWR spent fuel Into CANDU) fuel cycle plausible. The idea basically stems from that fissile isotope inventory in the discharged PWR spent fuels (~1.5w/o) is more than that in the natural uranium (~0.7w/o) which is used as CANDU reactor fuel.

In DUPIC process first step is to separate burned UO_2 fuel from 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 this main process UO_2 residuals on the decladded hull should be removed in conformity with the requirement or criteria that 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. A part of the remainder will be present as adherent dust and some may also be chemically bonded to the zirconium oxide layer on the inside of the fuel pin. Therefore, another process for additional removal of the last portion of the fuel is required, which also removes alpha contamination from the clad to a level qualifying the fuel hulls as non-TRU waste.

As one of the proposed secondary processes a plasma etching technique using fluorine containing gas is being investigated since the process satisfies the restrictive condition that whole DUPIC fuel manufacturing process is supposed to be dry and remote-controllable. For current research, CF_4/O_2 mixture gas plasma is used since the high reactivity of uranium compound with fluorine is well-known.

2. 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) higher fluoride, UF_5 and UF_6, formation should be suppressed in favor of UF_4 and atomic fluorine formation [3,4]. However, in these studies the elucidation of reaction mechanism was limited since they were overall reactions in equilibrium or in quasi-equilibrium.

Machiels and Olander performed a kinetic study on the reaction of UO_2 with F_2 by modulated molecular beam mass spectrometry and found that reaction product is UF_4 and the reaction probability is higher than 10^{-2} [5]. Authors claimed that reaction mechanism is a second order surface reaction coupled with double diffusion process. Their results, however, should be carefully extrapolated to that of the reaction 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 process in the semi-conductor industry is CF_4/O_2 mixture gas. Consequently a number of studies on the gas phase reaction of the mixture plasma 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 O_2 content in the feed gas [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, gas flow rate, distance between electrodes, etc.

Recently Martz examined the etching rate of Pu and PuO_2 by the same mixture gas plasma [7]. He found that it is a few Å/sec for the etching of Pu metal 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 tube and r. f. power of 50W was applied by wound electrical coil outside.

3. Experimental

The apparatus for UO_2 etching reaction with CF_4/O_2 mixture gas plasma is designed and manufactured to meet the experimental purposes (Figure 1). Maximum 4″ diameter disk or wafer-like sample can be heated up to 800℃ by an

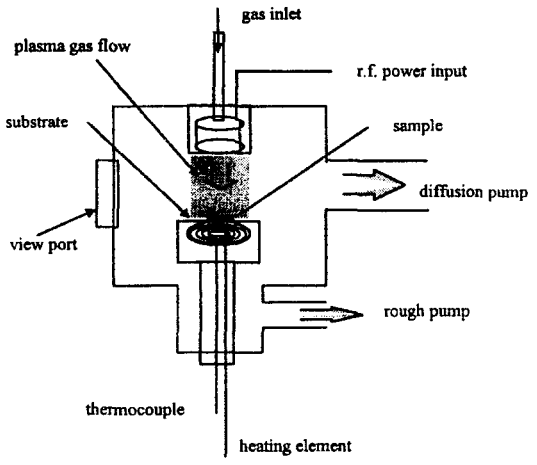

Fig. 1. Schematic of Plasma Etching Apparatus

electrical heater in the reaction chamber, in which r. f. power is applied up to 600W. Mass flow controllers fine-control the flow rates of CF_4 and O_2 gas and mix them before they reach the reaction chamber. Plasma gas pressure is controlled by the total flow rate of mixed gas while O_2 mole fraction is varied. Distance between parallel electrodes can be adjusted up to 10 cm, however, it remains stationary during current experiments.

In the experiments thin disks of natural uranium dioxide cut out of a pellet are used as specimens. Prior to the reaction, they are polished by grit 600 sandpaper and cleaned by ultrasonic cleaner. They are baked at 200℃ for 10 minutes in a ultra-high vacuum to evaporate the adsorbed moisture on the surface.

Etching reaction rate is determined by weight loss measurement before and after the reaction with an electro-micro balance whose sensitivity limit is 10^{-5}g.

4. Results and Discussion

In the experiments total gas pressure is maintained at 0.3 Torr while CF_4/O_2 ratio is varied and r. f. plasma power is applied only up to 150W because of temperature control difficulties due to internal heating of the chamber.

First, under the r. f. power of 100W etching reactions are examined at 210 ℃ substrate temperature with various CF_4/O_2 ratios. Exposure duration is 100 minutes. The rate is estimated with following formula:

$$\frac{(N_o/M)}{(N_o\rho M)^{2/3}}\ \frac{\omega}{At}\ \text{(monolayers/min.)} \qquad (1)$$

where N_o is Avogadro' s number, M is UO_2 atomic mass (270.03 g/mole), ρ is UO_2 density (10.96 g/cm^3), A is the area of the sample, w is the weight loss due to etching reaction, and t is exposure duration to plasma.

Whole experiments are repeated at several substrate temperatures up to 370℃ and the results are plotted in Figure 2.

In the figure, it is revealed that there exists an optimum CF_4/O_2 ratio for the reaction and it is around 4:1 at all temperatures under 370℃. While the background reaction rates outside the optimum composition remain almost same, more or less than 200 monolayers/min., peak rates increase with increasing substrate temperatures. In order to confirm the optimum gas composition at different plasma configuration additional examinations with finely-varied gas composition are also carried out and result in identical conclusion (closed symbol data in Fig. 2).

Experiments are repeated with higher r. f. power, 150W, and lower power, 50W, to see the rate enhancement. Even at r. f. power of 50W reaction rate peaks at the optimum composition are noticeable, however, all the rates at outside the composition are indiscernible, below 100 monolayers/min., at various temperatures. This means that at this power plasma is not developed in the gas mixture enough to promote continuous

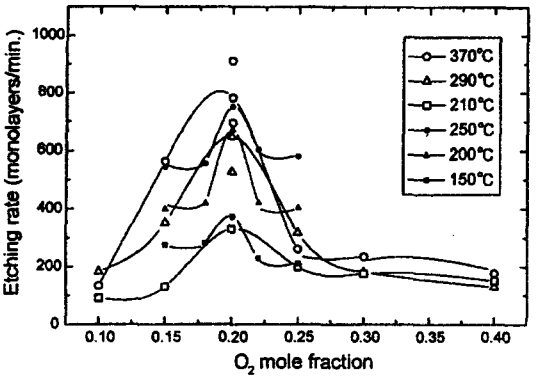

Fig. 2. Etching Rate vs. O_2 Mole Fraction at 100W

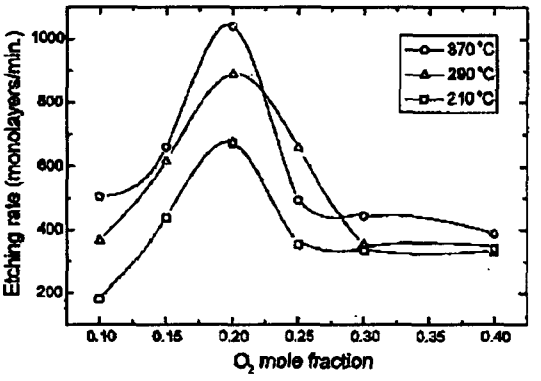

Fig. 3. Etching Rate vs. O_2 Mole Fraction at 150W

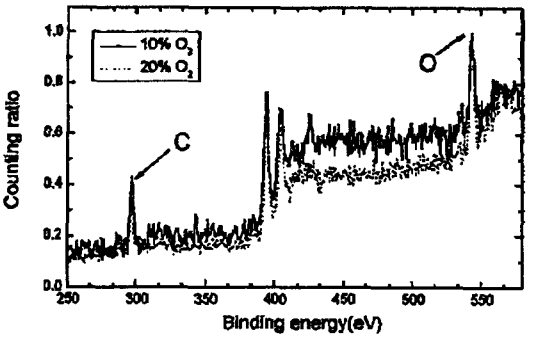

Fig. 4. XPS Results in Relative Intensity to Oxygen Peak Intensity

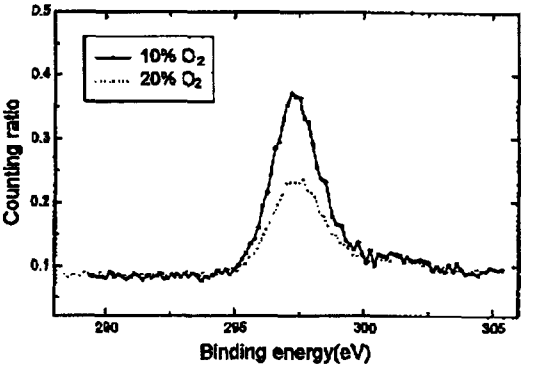

Fig. 5. Carbon Peaks in Detail in the Previous XPS Results

overall surface reaction because of low power.

Figure 3 shows the results at r. f. power of 150W. Reaction rate peaks are vividly observed at all temperature under 370℃ and they increase with increasing temperature. They are higher and broader than those at the same temperature under lower r. f. power. Highest rate reaches 1050monolayers/min. at 370℃, which is equivalent to about 0.5μm/min.

In the experiments, oxygen gas is injected in the feed gas to pick up the carbon atoms by forming volatile species such CO or CO_2 since it is fundamentally believed that fluorine atoms or fluorine containing radicals react with surface U atoms, and carbon residuals decomposed from carbon tetra-fluoride deposit on the surface then suppress surface reaction. In this respect, the existence of the optimum composition for fully developed surface reaction is understood. That is, at lower gas composition than the optimal one the surface reaction is suppressed due to the carbon residuals, on the other hand, at higher gas composition higher reactivity of oxygen with uranium atom than that with carbon may prevent from the formation of volatile reaction products such as uranium tetra- or hexa-fluorides.

The carbon pick-up by oxygen atoms is confirmed by XPS (X-ray Photoelectron Spectroscopy)

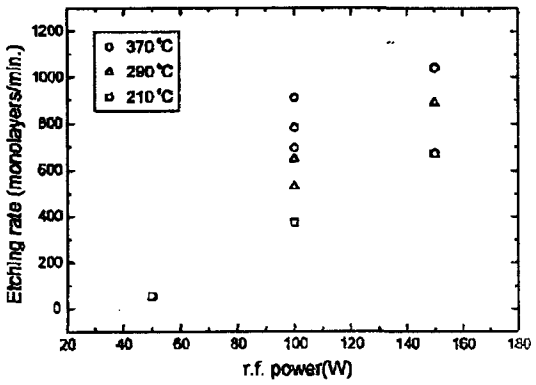

Fig. 6. UO_2 Etching Rate vs r.f. Power at 20% O_2 Mole Fraction

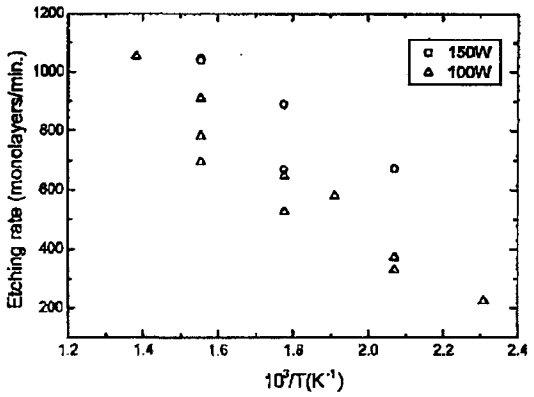

Fig. 7. UO_2 Etching Rate vs r.f. Substrate Temperature at 20% O_2 Mole Fraction

analysis of surface atom concentration in Figure 4. The figure shows that surface carbon concentration on the reacted surface at the optimum composition is much lower than that at non-optimum composition (10% O_2). The carbon peaks on both surfaces are shown in detail in Figure 5, in which carbon intensity on the former surface is only one third of that on the latter surface. The postulation of the higher reactivity of oxygen atom with uranium atom than that with carbon atom will be confirmed in the following experiments.

It is found that the etching rates are almost linearly proportional to r. f. power (Figure 6) and also increasing with increasing substrate temperature (Figure 7), thus, the etching rate will rise much higher if the reaction takes place at higher substrate temperature under more power applied. Figure 7 shows that this reaction may be an activated process, therefore, more experimental data will be generated to draw the activation energy on the process.

The overall reaction in this study is believed to produce uranium tetra- or hexa-fluorides along with carbon mono- or dioxide. They will be detected by using quadrupole mass spectrometer in the following experiments and UO_2 stoichiometry change and surface modification will be studied further.

5. Conclusions

From current experiments it is found that there exists an optimum CF_4/O_2 ratio for the maximum etching reaction of UO_2 with CF_4/O_2 mixture gas plasma and that it is around 4:1 at all temperatures up to 370℃. The role of oxygen atoms, the pick-up of carbon residuals on the surface, is confirmed by surface analysis using XPS (X-ray Photoelectron Spectroscopy).

Peak reaction rate at the optimum gas composition increases with increasing temperature as an activated process. Highest reaction rate obtained in this experiments reaches 1050 monolayers/min. at 370℃ under r. f. power of 150 W, which is equivalent to about 0.5 μm/min. These peaks are higher and broader than those at the same temperature under lower r. f. power.

At low r. f. power below 50W gas plasma does not seem to develope enough to promote overall surface reaction. Above the power reaction rate increases with increasing r. f. power.

Therefore, it is believed that higher power and higher substrate temperature raises the etching reaction rate further, which implies that this plasma processing of UO_2 is compatible as a secondary process for DUPIC process.

The overall reaction products, uranium tetra- or hexa-fluoride, will be identified by mass spectrometry and more data will be produced to determine the activation energy in this reaction in the following research.

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