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Surface Reaction of Uranium Dioxide with CF_4/O_2 r. f. Plasma

Yong-soo Kim*[1], Jin-young Min[1], Ki-kwang Bae[2], In-ha Jung[2] and Myung-seung Yang[2]
[1]Nuclear Engineering Department, Hanyang University
[2]Korea Atomic Energy Research Institute

1. Introduction

The fluorination of UO_2 has been extensively studied in the application-oriented fields such as uranium separation, processing, and conversion. Along with the applied research, fundamental studies of the UO_2/F_2 reaction have been reported by several authors [1-4].

Recently the feasibility of burning spent PWR fuel in a CANDU reactor was carried out. In the proposed process decladding of spent fuel pins and dry-processing of burned UO_2 such as OREOX (Oxidation and REduction of OXide fuel) process are the main processes to make re-sinterable fuel powder [5]. Most candidate mechanical decladding techniques were unable to recover more than 98 to 99.5% of the heavy metal/metal oxide. Thus, a plasma processing technique using fluorine containing gas plasma is proposed as a secondary decontamination process and its applicability is demonstrated [6].

For current research, the reaction rates of UO_2 in CF_4/O_2 r. f. plasma are determined at temperatures of up to 370℃ under total pressure of 0.3 Torr. The reaction rates are investigated as functions of CF_4/O_2 ratio, plasma power, substrate temperature, and exposure time to the plasma. The overall reaction mechanism is investigated in detail.

2. Experimental

The apparatus for UO_2 etching reaction with CF_4/O_2 r. f. plasma is designed and manufactured to meet the experimental purposes. The plasma reactor is a diode type and r. f. power of up to 600W is applied between the parallel electrodes, and sample substrate can be heated up to 800°C by the electrical heater in the reaction chamber. In the experiments thin disks of natural uranium dioxide cut out of a pellet are used as specimens.

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. Reactants and generation of reaction products are *in-situ* detected by the quadrupole mass spectrometer sitting in the detection chamber and identified by a PC-controlled data acquisition system.

3. Results and Conclusions

From the current investigation it is found that there exists an optimum CF_4/O_2 ratio for the efficient etching of UO_2 in CF_4/O_2 plasma regardless of r. f. power and substrate temperature. The ratio is around 4 under the substrate temperature of 370℃. At oxygen gas compositions of lower than the optimum, XPS analysis demonstrates that the amount of oxygen is not enough to pick up the carbon residuals, hence, the residuals decomposed from carbon tetra-fluoride may deposit on the surface and suppress surface reaction. On the other hand, at higher oxygen gas compositions, XRD analysis conforms that high reactivity of excessive oxygen with a surface uranium atom may form hyper-stoichiometric uranium oxides instead of carbon mono- or dioxide and interfere with the formation of volatile uranium fluorides. The highest etching reaction rate at 370℃ under 150W exceeds 1000 monolayers/min., which is equivalent to 0.4 μm/min. and comparable to that of the Si wafer in the semi-conductor industry.

According to the mass spectrometry, it is revealed that the major reaction product is uranium hexa-fluoride UF_6. Therefore, based on the experimental results the dominant overall reaction of uranium dioxide in CF_4/O_2 plasma is determined:

$$UO_2 + 3/2\ CF_4 + 3/8\ O_2 = UF_6 + 3/2\ CO_{2-x},\ (\text{where } x = 0 \text{ or } 1)$$

XPS analysis confirms that UO_2F_2 compound forms on the surface during the reaction as a primary intermediate and additional experiments show that reaction kinetics follows a linear rate law.

Therefore, it is concluded that the overall reaction of this fluorination of uranium dioxide in CF_4/O_2 plasma is rate-determined by the surface reaction between the uranium atom in UO_2F_2 intermediates on the surface and incoming fluorine atoms or fluorine containing radicals. The activation energy of this reaction is derived as 12.1 kJ/mole, which is comparable to 10.4 kJ/mole for Si and 15.8 kJ/mole for SiO_2.

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