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Plasma etching behavior of Y_2O_3 ceramics: Comparative study with Al_2O_3

Yu-Chao Cao[a,c], Lei Zhao[a], Jin Luo[a], Ke Wang[a,*], Bo-Ping Zhang[c], Hiroki Yokota[b], Yoshiyasu Ito[b], Jing-Feng Li[a,*]

[a] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, 100084 Beijing, PR China
[b] TOCALO Co., Ltd., R & D Laboratories, 674-0093 Hyogo, Japan
[c] School of Materials Science and Engineering, University of Science and Technology Beijing, 100083 Beijing, PR China

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ABSTRACT

The plasma etching behavior of Y_2O_3 coating was investigated and compared with that of Al_2O_3 coating under various conditions, including chemical etching, mixing etching and physical etching. The etching rate of Al_2O_3 coating declined with decreasing CF_4 content under mixing etching, while that of Y_2O_3 coating first increased and then decreased. In addition, the Y_2O_3 coating demonstrated higher erosion-resistance than Al_2O_3 coating after exposing to fluorocarbon plasma. X-ray photoelectron spectroscopy (XPS) analysis confirmed the formations of YF_3 and AlF_3 on the Y_2O_3 and Al_2O_3 coatings, respectively, which acted as the protective layer to prevent the surface from further erosion with fluorocarbon plasma. It was revealed that the etching behavior of Y_2O_3 depended not only on the surface fluorination but also on the removal of fluoride layer. To analyze the effect of porosity, Y_2O_3 bulk samples with high density were prepared by spark plasma sintering, and they demonstrated higher erosion-resistances compared with Y_2O_3 coating.

1. Introduction

Fluorocarbon plasmas have been extensively used in semiconductor industry in order to etch silicon wafers as well as clean processing chambers [1,2]. However, the fluorocarbon plasmas also bombard and erode inner-wall materials of the equipment, [3,4] while the resultant particles may contaminate the wafers and shorten the lifetime of the equipment. In order to protect the devices from erosion and the formation of contaminants, many oxide ceramics, such as Al_2O_3 and SiO_2, are used as anti-plasma-etching inner-wall materials [5–9]. Erosion of Al_2O_3 or SiO_2 coatings is, nevertheless, getting more serious due to the enhanced power application in the plasma equipment. Yttrium oxide (Y_2O_3), featured by a much lower etching rate, has been increasingly proposed as potential plasma-sprayed coatings, especially in semiconductor and solar cell fabricating industry [9–13].

The etching mechanism of silicon-based materials under fluorine-based plasma has been extensively investigated in terms of resultant products. The formation of top carboneous polymer layer as well as the SiF_xO_y reaction layer has been identified, which depends on the etching conditions and the etched materials [14–17]. The polymer layer has an influence on the etching rate by reducing kinetic energy of the plasma during etching process [18]. And the thickness of the polymer layer is mainly determined by three factors: deposition rate of the polymer layer, consumption rate of the substrate etching, and removal rate of certain volatile products. Standaert et al. [17] reported that the etching rate of SiO_2, Si_3N_4, and Si declines as a function of the fluorocarbon layer thickness, suggesting that the fluorocarbon layer is indeed an etch-inhibiting layer. However, the etching mechanism of yttrium-based materials is still not well established.

In the current study, the etching behavior of Y_2O_3 under fluorocarbon plasmas was investigated. As a comparison, the etching behavior of Al_2O_3 was also studied. The Al_2O_3 and Y_2O_3 coatings were prepared by atmospheric plasma spraying. The dense Y_2O_3 bulks prepared by spark plasma sintering were used to analyze the effect of porosity. The formations of YF_3 and AlF_3 on Y_2O_3 and Al_2O_3 coatings after exposed to plasmas with different CF_4 contents were confirmed, respectively. The fluoride on the surface acted as protection layer to prevent Y_2O_3 and Al_2O_3 coatings from further reacting with plasma. It should be noted that etching rate of Y_2O_3 was lower than that of Al_2O_3 due to the much lower sublimation temperature of yttrium fluorides than that of aluminum fluoride.

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* Corresponding authors.
E-mail addresses: jingfeng@mail.tsinghua.edu.cn (J.-F. Li), wang-ke@mail.tsinghua.edu.cn (K. Wang).

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2. Experimental procedures

Commercially available Y_2O_3 (99.99%, $d_{50} = 25\ \mu m$) and Al_2O_3 (99.99%, $d_{50} = 25\ \mu m$) particles were used as raw materials to prepare the sprayed coatings using atmospheric plasma spraying (APS). Al alloy plates (JIS: A5052, 20 mm × 20 mm × 2 mm) were used as the spraying substrate. During the spraying process, the flux of primary gas (Ar) was controlled at $4.5 \times 10^{-2}\ m^3$/min and the secondary gas (H_2) was $7 \times 10^{-3}\ m^3$/min, with an arc current of 570 A and an arc voltage of 67 V. The thickness of the sprayed coating was about 300 μm with a roughness less than 0.2 μm after being polished. The density of sprayed Al_2O_3 and Y_2O_3 coated layers was 3.5 g/cm^3 and 4.7 g/cm^3, which was determined by the Archimedes method after being desquamated from the Al alloy substrate. The Y_2O_3 (99.99%, $d_{50} = 7.21\ \mu m$) powders were sintered by spark plasma sintering (SPS) first at 1173 K for 5 min under a uniaxial pressure of 30 MP, and then at 1873 K for 10 min under 50 MP. The SPS-sintered bulks showed good transparency and high density of 4.97 g/cm^3, which were polished to 1 mm for afterwards plasma etching.

The plasmas etching was performed by an inductively coupled plasma (ICP) etcher (RIE-101iPH, SAMCO, Japan) at the same electrical bias with different processing gases (Ar, CF_4 and O_2). Fig. 1 shows schematic illustration of cross section of ICP etcher. Details of the etching conditions were shown in Table 1. Three different treatment conditions, i.e. chemical etching (CE), mixing etching (ME) and physical etching (PE), were carried out to study the etching behavior. "Before etching" was abbreviated as "BE" in the following paragraph. The transmittance of the SPS-sintered samples before and after etching was measured by ultraviolet-visible spectrophotometer (Lambda 950, Perkin Elmer, America). The etched depth was measured by a laser microscope (VK-9700, KEYENCE, Japan), and the surface microstructure was observed by field emission scanning electron microscopy (FE-SEM, LEO1530, Germany). Electron backscattered diffraction (EBSD) analysis on the cross-section of ME condition etched samples was performed. X-ray photoelectron spectrum (XPS, ESCALAB 250 Xi, England) analysis was performed by a monochromatic Al Kα X-ray source at a passing energy of 20 eV with a 650 μm spot size. Due to the insulation nature of specimens, the measurement was conducted using an electron flooding gun to prevent peak position shift induced by the specimen surface charge. Focused Ar$^+$ ions' sputtering was carried out to investigate the chemical compositional depth profiling. The spectrum of the etched surface without sputtering was fitted with fixed peak position spacing, peak area ratio, full width at half maxima (FWHM) and Gaussian–Lorentzian ratio. The peak position was calibrated with the binding energy of the C 1S peak (284.8 eV) obtained from the same surface spectrum.

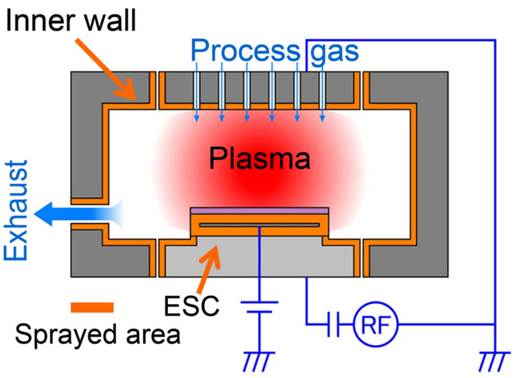

Fig. 1. Schematic illustration of the cross section of inductively coupled plasma (ICP) etching tool.

3. Results and discussion

The cross section and surface microstructures of Y_2O_3 and Al_2O_3 coatings before etching are shown in Fig. 2. Both of them have a porous microstructure with density of 4.7 g/cm^3 and 3.5 g/cm^3, respectively. The erosion-resistance of Y_2O_3 and Al_2O_3 coatings was measured after exposure to the plasma with various mixing ratios of gas flow.

Fig. 3 shows the dependence of the etching rate on the mixing ratio of gas flow, and Si crystal was used as the reference. With decreasing CF_4 content in the gas flow, the etching rate of Si crystal as well as Al_2O_3 coating declined significantly. Since the dissociated F radicals from CF_4 could promote chemical reaction and yield volatile species with various atoms including Si and Al, resulting in decreased etching rate of Si crystal and Al_2O_3 coating with decreasing CF_4 content. However, the etching rate of Y_2O_3 coating increased to a peak value when CF_4 decreased to 45 sccm (standard-state cubic centimeter per minute), and it slightly declined as CF_4 further decreased. It was found that Y_2O_3 coating had excellent erosion-resistance when exposed to CE condition compared with Si crystal and Al_2O_3 coating as shown in Fig. 3. The etching rate of sprayed Y_2O_3 coating was only one fifth of Al_2O_3 coating, and one twelfth of Si crystal. However, all these three materials had nearly equal etching rate when being etched under PE condition, which could be attributed to the equal bombardment effect of Ar plasma on the materials that accelerated by the bias voltage [12].

The surface microstructures of Y_2O_3 and Al_2O_3 coatings after etching in CE, ME and PE conditions for 45 min are shown in Fig. 4, respectively. Obvious erosion phenomenon was observed on the etched surfaces of Y_2O_3 and Al_2O_3 coatings (Fig. 4a–c). There were no obvious differences among etched Y_2O_3 coating surfaces under three etching conditions. The erosion of Al_2O_3 coating was severer than that of Y_2O_3 coating after exposing to both CE and ME conditions, which indicated different etching rates for Al_2O_3 and Y_2O_3 coatings. Severer erosion on Al_2O_3 coating surface was observed under CE and ME conditions than PE condition.

In order to analyze the effect of porosity, Y_2O_3 bulk sample with a high density of 4.97 g/cm^3 was prepared. The erosion-resistance of sprayed Y_2O_3 coating and Y_2O_3 bulk sample was compared in Table 2. The etching rate of SPS-sintered bulk decreased by 30.7%, 39.9% and 45.7% than that of the thermal sprayed Y_2O_3 coating when etched under CE, ME and PE, respectively, indicating

Table 1
Details of the plasma etching conditions.

Etching conditions		Chemical etching (CE) CF_4 rich	Mixing etching (ME)	Physical etching (PE) Ar rich
ICP power	W		800	
Bias power	W		450	
Gas flow				
$Ar:CF_4:O_2$	SCCM[a]	0:95:5	50:45:5	95:0:5
Total	SCCM		100	
Exposure time	min		45	

[a] Standard-state cubic centimeter per minute.