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Etch damage characteristics of TiO_2 thin films by capacitively coupled RF Ar plasmas

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ABSTRACT

Etch damage of TiO_2 thin films with the anatase phase by capacitively coupled RF Ar plasmas has been investigated. The plasma etching causes a mixed phase of anatase and rutile or the rutile phase. The effect of Ar plasma etching damage on degenerating TiO_2 thin films is dependent on gas pressure and etching time. The physical etching effect at a low gas pressure (1.3 Pa) contributes to the degradation: the atomic O concentration at the thin film surface is strongly increased. At a high gas pressure (13–27 Pa) and long etching time (60 min), there are a variety of surface defects or pits, which seem to be similar to those for GaN resulting from synergy effect between particle and UV radiation from the plasmas. For the hydrophilicity, the thin film etched at the high gas pressure and a short etching time (5 min) seems to have no etch damage: its contact angle property is almost similar to that for the as-grown thin film, and is independent of the black light irradiation. This result would probably result from formation of donor-like surface defects such as oxygen vacancy.

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1. Introduction

TiO_2 thin films have received much attention as the excellent photo-catalytic materials with non-toxicity and chemical stability for applications in water and air purification under the UV light irradiation [1–3]. This is because TiO_2 thin films are more recuperative and practical than fine TiO_2 powders.

As for the thin film deposition, the DC reactive planar magnetron sputtering system, in which plasmas are used to emit atoms from a target material, is one of the promising techniques for uniform and large-areas coating. However, plasma-induced damage to TiO_2, which means degradation of structural quality of the thin film such as spatial disorder and surface roughness, is a crucial issue in the sputtering system. The plasma-induced damage significantly degrades the original photo-catalytic properties as a result.

In this study, etch damage characteristics of TiO_2 thin films by Ar plasmas have been investigated using a capacitively coupled RF plasma reactor with an asymmetric electrode system (CPA) and a modeling of plasma–surface interactions (PIS). Emphasis is put on a change in the atomic O concentration, surface morphology, RMS surface roughness and XRD pattern of TiO_2 thin films etched for a variety of gas pressures and etching times. The change in the hydrophilicity is also described. The change in etching yields of O and Ti by Ar^+ from TiO_2, calculated by PIS, is described in association with the experimental data.

2. Experiment and modeling

A CCP reactor with an asymmetric electrode system (CPA) was employed for the Ar plasma etching of TiO_2 [4]. The distance between two SUS304 electrodes is 4 cm. TiO_2 thin films are placed on the cathode 80 cm^2 in area, which is powered by a 13.56 MHz RF generator. The anode 1217 cm^2 in area is electrically grounded. CPA is characterized by a result that the self-bias voltage $|V_{DC}|$ generated at the cathode is equal to the RF maximum voltage V_{RF}, $V_{DC} = -V_{RF}$. In this study, V_{RF} was set to 200 V. The gas pressure was varied from 1.3 to 27 Pa while the gas flow rate was kept 15 mL/min. The RF power was increased from 5 to 40 W with increasing gas pressure from 1.3 to 27 Pa. The specimen used was a TiO_2 thin film deposited on unheated Corning #1737 glass ($50 \times 50 \times 1.1$ mm^3) using the DC facing target planner magnetron sputtering [5]. The deposited thin film has the anatase (101), (112) and (211) XRD pattern, whose thickness is ~ 1 μm.

After the plasma etching, the atomic O concentration at the etched TiO_2 was measured using EDX (SHIMADZU EDX-800). The surface morphology and RMS surface roughness (5 μm^2 in area) were observed using SEM (JEOL JSM-6390HV) and AFM (SII SPA-

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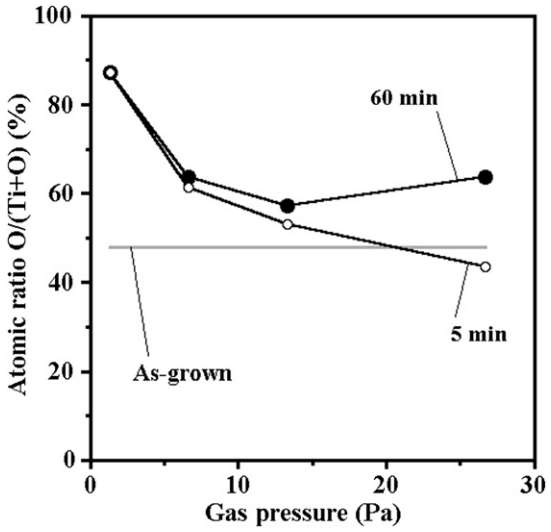

Fig. 1. Dependence of the atomic O concentration at the etched TiO_2 thin film surface on gas pressure for different etching times. The gray line corresponds to the result for the as-grown TiO_2 thin film.

300), respectively. The crystal structure was determined using XRD (Rigaku Rint-2100). For the hydrophilicity evaluation, the contact angle of deionized water (2 μL) was measured under the 1 mW/cm^2 UV light irradiation, using Drop Master (Kyowa Interface Science CA-V200). The UV light source is a commercial black light lump. The contact angle was also measured without UV light irradiation.

PIS simulation has been developed to understand the physical etching of TiO_2 by Ar plasmas. PIS is based on particle models of the discharge plasma, PIC/MCS [6], and the physical etching, BCA/MCS [7]. Both the self-consistent Ar discharge plasma behavior and the physical etching of TiO_2 by Ar^+ plasma ions impinging on the surface are analyzed by PIS. For this study, the etching yields of O and Ti, Y_O and Y_{Ti}, are represented.

In the discharge plasma model, movement of e^- and Ar^+ is subjected to Newton forces of their own field and applied RF field that are obeyed by the Poisson law. During the movement the elastic, exciting, and ionizing reactions of e^- with Ar gas are assumed to occur [8]. For Ar^+, there are their elastic and charge exchange reactions with Ar gas [9]. In the physical etching model, the impinging Ar^+ plasma ions move in TiO_2, receiving their elastic energy loss with solid atoms (Ti and O) and their inelastic energy loss with solid electrons [10–12]. This calculation is repeated until

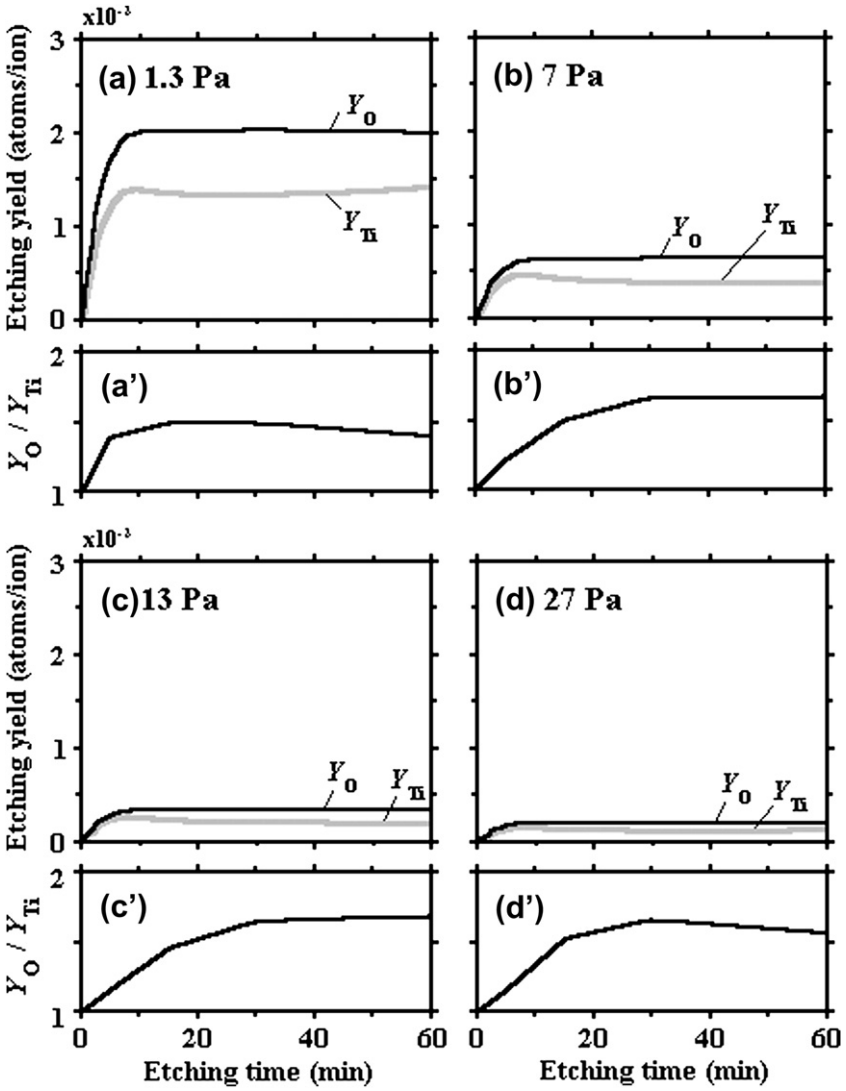

Fig. 2. Calculated etching yields of O and Ti from TiO_2 by Ar^+ plasma ions as a function of etching time for a variety of gas pressures. Fig. (a′)–(d′) show the ratios of etching yield of O to Ti, Y_O/Y_{Ti}, for the different gas pressures.

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