Characteristics of TiO₂ Surfaces Etched by Capacitively Coupled Radio Frequency N₂ and He Plasmas

Retsuo Kawakami¹, Masahito Niibe², Yoshitaka Nakano³, Masashi Konishi¹, Yuta Mori¹, Hideo Takeuchi⁴, Tatsuhiro Shirahama¹, Tetsuya Yamada¹, and Kikuo Tominaga¹

¹The University of Tokushima, 2-1 Minami-Josanjima, Tokushima 770-8506, Japan
²University of Hyogo, 3-1-2 Kouto, Kamigoori, Ako-gun, Hyogo 678-1205, Japan
³Chubu University, 1200 Matsumoto, Kasugai, Aichi 487-8501, Japan
⁴The University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522-8533, Japan

E-mail: retsuo@ee.tokushima-u.ac.jp

Abstract. We have investigated characteristics of anatase TiO₂ thin film surfaces etched by a capacitively coupled radio frequency N₂ plasma from the viewpoint of both an experiment and a simulation. The result obtained with use of the N₂ plasma is compared with that obtained with use of the He plasma. The experimental O/Ti ratio at the surface etched by the N₂ plasma increases as a function of etching time. The increase in the experimental O/Ti ratio is independent of a change in gas pressure. The above-mentioned experimental results agree with the simulation result that the Ti atoms at the surface are preferentially removed by N₂⁺ ions. The experimental O/Ti ratio at the surface etched by the He plasma also increases, which does not agree with the simulation result that the O atoms are preferentially removed by He⁺ ions. The O-1s XPS spectra of the surface etched by the He plasma show the peak associated with oxygen and water adsorbed by the surface. In the case where the component of the adsorbed oxygen and water in each spectrum is subtracted, the experimental O/Ti ratio at the surface etched by the He plasma shows a decrease. This is consistent with the simulation result. The adsorption of oxygen and water seems to be caused by ambient air. Morphology of the surface etched by the N₂ plasma is almost similar to that of the as-grown surface regardless of the changes both in etching time and in gas pressure. In contrast, morphology of the surface etched by the He plasma changes as the etching time increases. This result is independent of the gas pressure.

1. Introduction

TiO₂ has been attracting much attention for applications to dye-sensitized solar cells [1,2] and environmental cleaning [3-5]. The attention to TiO₂ originates from the fact that TiO₂ has excellent photo-catalytic properties, non-toxicity, and chemical stability. In order to prepare TiO₂ thin films, sputtering is one of the promising deposition techniques for uniform and large area coating [6-8]. However, plasma-induced damage of TiO₂, which degrades the original characteristics, is a crucial problem because plasmas are used to sputter atoms from a target surface [9]. TiO₂ has also been expected for a candidate of gate dielectric material in metal-oxide-semiconductor transistors [10-12].
The expectation arises from the characteristic that TiO$_2$ has a high dielectric constant, which results in suppressing of the gate leakage current. However, the damage of TiO$_2$ in the plasma etching process is also a crucial problem because TiO$_2$ is a binary compound [13]. It is, therefore, necessary to study the above-mentioned issue in order to improve the characteristics of TiO$_2$ surfaces exposed to or etched by various types of plasmas.

So far, Kawakami et al. have studied He plasma-induced damage of TiO$_2$ [14]. Their study indicates that morphology of the etched surface changes at the gas pressure range from 10 to 100 mTorr as the etching time increases to 60 min. It is considered that the change in the surface morphology results from synergy effect of He$^+$ ions and ultraviolet (UV) light emitted from the plasma, i.e., UV irradiation effect [14]. The mechanism of the change in the surface morphology, however, has not been clarified in detail. Furthermore, it is not clear whether the surface morphology can be changed by other types of plasma.

In the present work, characteristics of TiO$_2$ thin film surfaces etched by a N$_2$ plasma have been studied using a capacitively coupled radio frequency (RF) plasma reactor. The surface morphology was observed, and O/Ti ratio at the surface was analyzed. A change in O/Ti ratio at the surface etched physically by N$_2^+$ ions was also calculated with a simulation model of plasma-surface interactions developed by the authors. The result obtained with use of the N$_2$ plasma is compared with that obtained with use of the He plasma. We discuss a difference between the surface characteristics induced by the N$_2$ and He plasmas.

2. Experiment and Simulation Procedures

For the present study, we employed a capacitively coupled RF plasma reactor with an asymmetric electrode system, named CPA: the area of anode electrode was much larger than that of the cathode one [14]. The cathode was powered with a 13.56 MHz RF generator (Peal Kogyo RP-500C). The anode, which is located 4 cm away from the cathode, was electrically grounded. The RF maximum voltage $V_{RF}$ was set to 200 V. The gas pressure was varied from 10 to 100 mTorr while the gas flow rate was kept to be 15 ml/min. The RF power of the N$_2$ plasma increased from 4 to 8 W with increasing gas pressure from 10 to 100 mTorr. The RF power for the He plasma was also enhanced from 5 to 10 W. The self-bias voltage $V_{DC}$ generated at the cathode in each plasma discharge was almost equal to $-V_{RF}$ regardless of the increase in the gas pressure: $V_{DC} \approx V_{RF} = -200$ V. Spectra of UV light emitted from the plasmas were measured using a spectroscope (Ocean Optics USB2000).

The specimen used was a thin film of TiO$_2$ deposited on unheated glass (Corning 1737) using the DC facing target planner magnetron sputtering technique [6]. The specimen was $\sim 1 \mu$m in thickness, and it showed the anatase (101) peak in the XRD pattern. The specimen was cut into the samples. After the plasma etching, the surface morphologies were observed using a scanning electron microscope (SEM, Hitachi S-4700). The O/Ti ratios at the etched surfaces were analysed with the O-1s and Ti-2p spectra taken using X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000).

In order to clarify the N$_2$ plasma etching of TiO$_2$, a simulation model for plasma-surface interactions, named PIS, has been developed. The developed simulation is composed of two particle models. One is a model for simulating the plasma discharge including reactions of charged particles with gas, which is based on PIC/MCS [15,16]. The other is a model for simulating the physical etching, which is based on BCA/MCS [17]. Both the self-consistent N$_2$ plasma behaviour and the physical etching by N$_2^+$ ions impinging on the surface of TiO$_2$ were analysed using PIS. In the model of plasma discharge, movement of charge particles, e$^-$ and N$_2^+$, which is dominated by the Newton and Poisson laws, was simulated [15]. The simulation takes account of the elastic, excitation, and ionizing reactions of e$^-$ with N$_2$ gas [16,18], as well as the elastic and charge transfer reactions of N$_2^+$ with N$_2$ gas [16,19]. As a result, a change in energy of the impinging N$_2^+$ ions with gas pressure was calculated. In the model of physical etching, the elastic and inelastic reactions of moving particles (N$_2$, Ti, and O) with target particles (Ti and O) and with electrons in the solid were simulated based on the same scheme as that used in BCA/MCS [17]. The surface binding energy, which is indispensable for emitting the target atoms from the surface, was assumed to be the TiO$_2$ binding energy, 5.5 eV [20].
Before the simulation starts, O/Ti ratio at the surface is set to be 2. Eventually, a change in the O/Ti ratio with an etching time was calculated. For the simulation of He plasma etching, the details are described in ref. 14.

3. Results and Discussion

Figure 1 shows energy of N\textsubscript{2}\textsuperscript{+} ions impinging on the cathode (the TiO\textsubscript{2} surface) as a function of gas pressure, which is calculated using the PIS simulation. The energy of N\textsubscript{2}\textsuperscript{+} decreases with increasing gas pressure. The decrease is due to an increase in the energy losses of N\textsubscript{2}\textsuperscript{+} resulting from its elastic and charge exchange reactions with N\textsubscript{2} [21]. The result for N\textsubscript{2}\textsuperscript{+} is almost similar to that for He\textsuperscript{+} as shown in Fig. 1. The similarity between the energies of N\textsubscript{2}\textsuperscript{+} and He\textsuperscript{+} originates from the fact that the self-bias voltages generated by the N\textsubscript{2} and He plasmas are almost the same. In contrast, the flux of N\textsubscript{2}\textsuperscript{+} increases with increasing gas pressure as shown in Fig. 1. The flux is roughly derived from experimental data of the RF plasma discharge [14]. The increase in the flux of N\textsubscript{2}\textsuperscript{+} almost resembles that of He\textsuperscript{+}. The flux of N\textsubscript{2}\textsuperscript{+} at each gas pressure, however, is lower than that of He\textsuperscript{+}. The lower flux of N\textsubscript{2}\textsuperscript{+} is probably because the N\textsubscript{2} plasma density, which is proportional to the flux, is lower than the He plasma density. The lower density of N\textsubscript{2} plasma is attributed to the phenomenon that reaction of vibration excitation of N\textsubscript{2} by electron impact is more pronounced than that of the ionization [18].

Figure 2 shows the spectra of UV light emitted from the N\textsubscript{2} and the He plasmas at various gas pressures. As shown in Fig. 2(a), at the low gas pressure of 10 mTorr, several peaks appear in the wavelength range from 310 and 390 nm. The observed peaks are assigned to N\textsubscript{2} second positive system band, 2P(\nu',\nu'')\rightarrow B\textsuperscript{2}T\textsubscript{2}(\nu''), where \nu is the vibrational state [22]. The result of the measurement on the UV spectra indicates the significant contribution of vibrationally excited N\textsubscript{2} to the emitted UV light. The peak positions do not change with increasing gas pressure, but their intensities slightly increase. In the emission spectra of the He plasma generated at the low gas pressure, few peaks appear between the wavelengths of 388 and 398 nm as shown in Fig. 2(b). The peaks are due to HeI transition lines, which indicates the contribution of excited He to the UV light [14]. The intensities of the peaks are enhanced with increasing gas pressure, and the peaks positions do not change. The spectra of UV light emitted from the N\textsubscript{2} and He plasma are, therefore, independent of gas pressure.
Figure 3 shows the experimental and calculated O/Ti ratios at the surfaces at various gas pressures. As shown in Figs. 3(a), 3(c), and 3(e), the experimental O/Ti ratio at each gas pressure increases with an increase in the etching time. The increase in the experimental O/Ti ratio agrees with the simulation that Ti atoms are preferentially removed by the physical etching effect resulting from the N$_2^+$ impact. The preferential etch of Ti atoms is attributed to the phenomenon that Ti atoms move more easily than O atoms by N$_2^+$ impact because, on the basis of a binary collision model, the maximum transferable elastic energy of N$_2^+$ to Ti is higher than that of N$_2^+$ to O [17]. The agreement between the experimental and simulated results indicates that the physical etching effect produces Ti vacancies on the etched surface regardless of the gas pressure. In general, it is considered that the Ti vacancies form acceptor levels above the valence band [23]. Thus, the etched surface has a possibility of exhibiting p-type conductivity.

As shown in Figs. 3(b), 3(d), and 3(f), the experimental O/Ti ratio for the He plasma (open circles) also increases with an increase in the etching time. The increase in the experimental O/Ti ratio is irrespective of gas pressure. The experimental O/Ti ratio does not agree with the simulated result that the calculated O/Ti ratio decreases with an increase in the etching time. The decrease in the calculated O/Ti ratio indicates that O atoms are preferentially removed by He$^+$ ions and that, as a result, the etched surface becomes a Ti-rich surface. The preferential etch of O atoms results from the phenomenon that O atoms move more easily than Ti atoms by He$^+$ impact, based on a binary collision model result that the maximum transferable elastic energy of He$^+$ to O is higher than that of He$^+$ to Ti [17]. In general, the O vacancies are considered to be donor-like defects in the near-surface region [24]. The simulation predicts that the etched surface has a possibility of exhibiting n-type conductivity.

The O-1s XPS spectra for the He plasma show the peak associated with oxygen bonding to titanium, as well as the peak related to oxygen and water adsorbed in the surface (not shown here), according to ref. 25. In the case where the component of adsorbed oxygen and water in each spectrum is subtracted, the experimental O/Ti ratio (solid circles) decreases. This is consistent with the calculated result as
shown in Figs. 3(b), 3(d), and 3(f). The adsorption of oxygen and water can be explained in terms of the following fact. The etched surface becomes a Ti-rich surface, as predicted from the simulation. The Ti-rich surface easily adsorbs oxygen and water in ambient air as the samples are taken out of the vacuum chamber. The agreement between the experimental and simulated results, therefore, indicates that the preferential etch of O atoms is independent of the gas pressure.

Figure 4 shows SEM images of the surfaces etched by the N$_2$ and the He plasmas at various gas pressures. As shown in Figs. 4(a)-4(c), morphology of the surface etched at each gas pressure is almost similar to that of the as-grown surface even as the etching time increases to 60 min. The result of the SEM measurement indicates that the surface morphology for the N$_2$ plasma is independent of the gas pressure and etching time, though the surface is irradiated with the emitted UV light. As shown in Figs. 4(d)-4(f), the surface morphology for the He plasma changes as the etching time increases to 60 min, as described in ref. 14, which indicates that the change in the surface morphology caused by the He plasma is dependent on the etching time and gas pressure.

The difference between the surface morphologies caused by the two kinds of plasma cannot be fully explained only in terms of the UV radiation effect [14]. The reason is indicated by the fact that the two kinds of plasma emit the UV light as shown in Fig. 2. The above-mentioned difference can be related to the sizes of atoms removed preferentially from the surface. It is known that the ionic radius of Ti$^{4+}$ (64 pm) is smaller than that of O$^{2-}$ (124 pm) [26]. Since Ti atoms are preferentially removed by the N$_2$ plasma as described above, pits with radii comparable to the radius of Ti are formed on the surface. It is difficult to observe the formed pits because their sizes are too small. The formed pits also disappear because of the structural relaxation to the stable crystalline configuration. As a result, it is observed that the surface morphology for the N$_2$ plasma is almost similar to that of the as-grown sample. In contrast, since O atoms are preferentially removed by the He plasma as described above, pits with radii comparable to the radius of O are formed on the surface. The formed pits remain because their radii are too large to be recovered by the structural relaxation. As a result, the surface morphology for the He plasma probably changes in association with the UV radiation effect [14]. Detailed study for the difference between the surface morphologies by the two kinds of plasma will be necessary in the future.

![Figure 4. SEM images of TiO$_2$ surfaces at various gas pressures. The etching time was 60 min.](image-url)
4. Conclusion

From the viewpoint of both the experiment and a simulation, we have been studied characteristics of TiO\(_2\) surfaces etched by the N\(_2\) plasma. The result obtained with use of the N\(_2\) plasma was compared with that of the He plasma. The experimental O/Ti ratio at the surface etched by the N\(_2\) plasma irrespectively increases with an increase in the gas pressure, which agrees with the simulation that Ti atoms are preferentially removed by N\(_2^+\) ions impinging on the surface. The experimental O/Ti ratio at the surface etched by the He plasma also increases, which does not agree with the simulation that O atoms are preferentially removed by He\(^+\) ions. The O-1s XPS spectra for the He plasma show the peak associated with oxygen and water adsorbed by the surface. As the component of the adsorbed oxygen and water in each spectrum is subtracted, the experimental O/Ti ratio for the He plasma decreases, which is consistent with the simulated one. The adsorption of oxygen and water seems to be caused by ambient air. The morphology of the surface etched with use of the N\(_2\) plasma is almost similar to that of the as-grown surface. This is independent of the etching time and gas pressure. In contrast, the morphology of surface etched with use of the He plasma changes as the etching time increases. This is independent of gas pressure.

5. References

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