Characteristics of TiO_2 Surfaces Etched by Capacitively Coupled Radio Frequency N_2 and He Plasmas

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Abstract. We have investigated characteristics of anatase TiO_2 thin film surfaces etched by a capacitively coupled radio frequency N_2 plasma from the viewpoint of both an experiment and a simulation. The result obtained with use of the N_2 plasma is compared with that obtained with use of the He plasma. The experimental O/Ti ratio at the surface etched by the N_2 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 N_2^+ 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 N_2 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

TiO_2 has been attracting much attention for applications to dye-sensitized solar cells [1,2] and environmental cleaning [3-5]. The attention to TiO_2 originates from the fact that TiO_2 has excellent photo-catalytic properties, non-toxicity, and chemical stability. In order to prepare TiO_2 thin films, sputtering is one of the promising deposition techniques for uniform and large area coating [6-8]. However, plasma-induced damage of TiO_2, which degrades the original characteristics, is a crucial problem because plasmas are used to sputter atoms from a target surface [9]. TiO_2 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 ~1 μm 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_2^+ ions impinging on the cathode (the TiO_2 surface) as a function of gas pressure, which is calculated using the PIS simulation. The energy of N_2^+ decreases with increasing gas pressure. The decrease is due to an increase in the energy losses of N_2^+ resulting from its elastic and charge exchange reactions with N_2 [21]. The result for N_2^+ is almost similar to that for He^+ as shown in Fig. 1. The similarity between the energies of N_2^+ and He^+ originates from the fact that the self-bias voltages generated by the N_2 and He plasmas are almost the same. In contrast, the flux of N_2^+ 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_2^+ almost resembles that of He^+. The flux of N_2^+ at each gas pressure, however, is lower than that of He^+. The lower flux of N_2^+ is probably because the N_2 plasma density, which is proportional to the flux, is lower than the He plasma density. The lower density of N_2 plasma is attributed to the phenomenon that reaction of vibration excitation of N_2 by electron impact is more pronounced than that of the ionization [18].

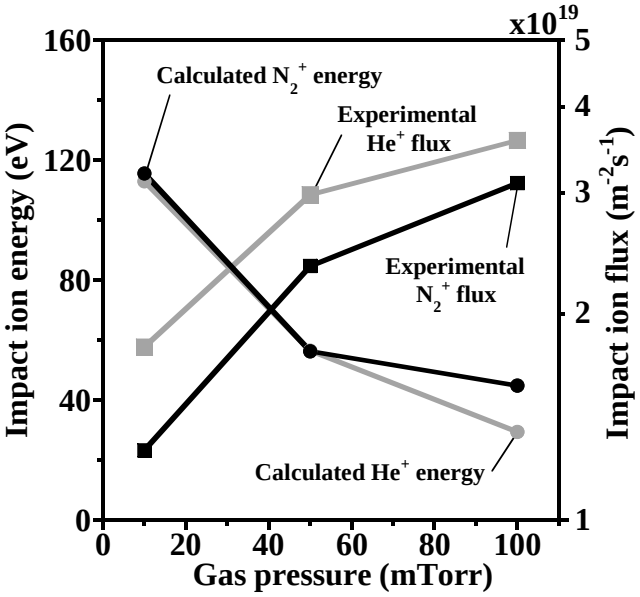

Figure 1. Energies and fluxes of N_2^+ and He^+ ions impinging on the cathode (the TiO_2 surface) as a function of gas pressure.

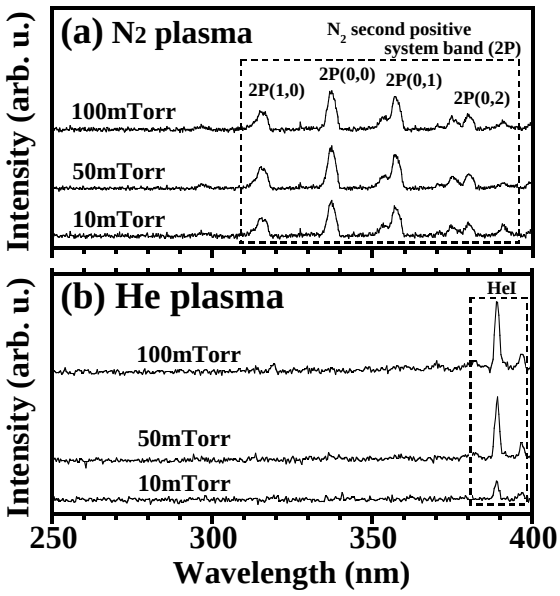

Figure 2. Spectra of UV light emitted from the plasmas generated at various gas pressures.

Figure 2 shows the spectra of UV light emitted from the N_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_2 second positive system band, $2P(v',v'')$: $C^3\Pi_u(v') \rightarrow B^3\Pi_g(v'')$, where v is the vibrational state [22]. The result of the measurement on the UV spectra indicates the significant contribution of vibrationally excited N_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_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.

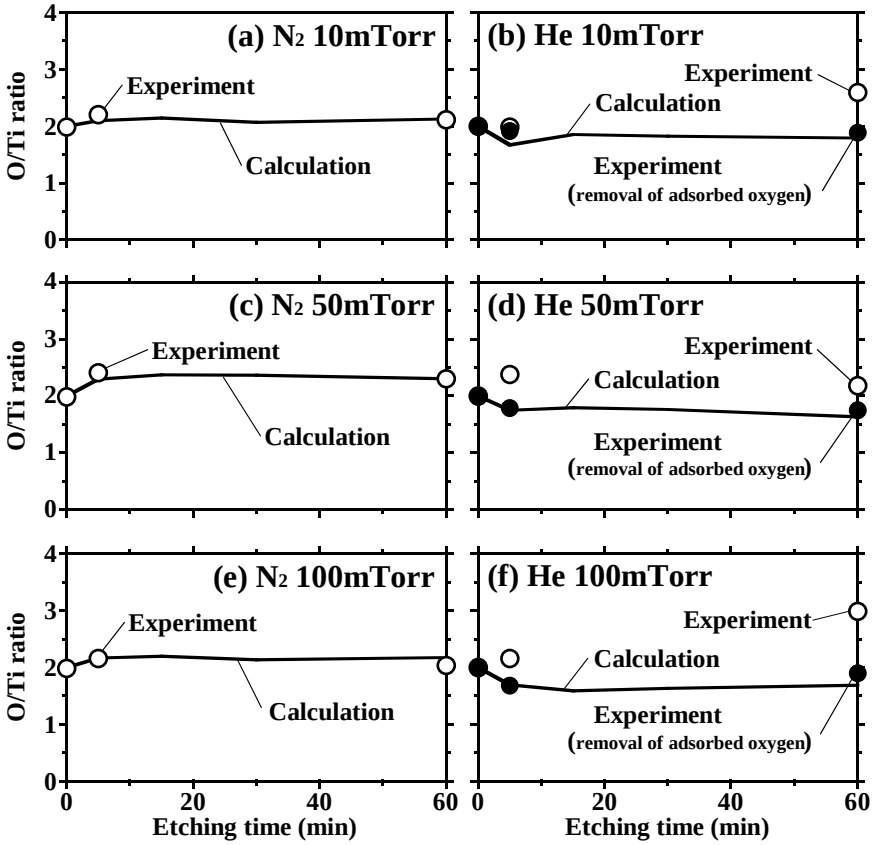

Figure 3. Experimental and calculated O/Ti ratios at the surfaces at various gas pressures, as a function of etch time.

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.

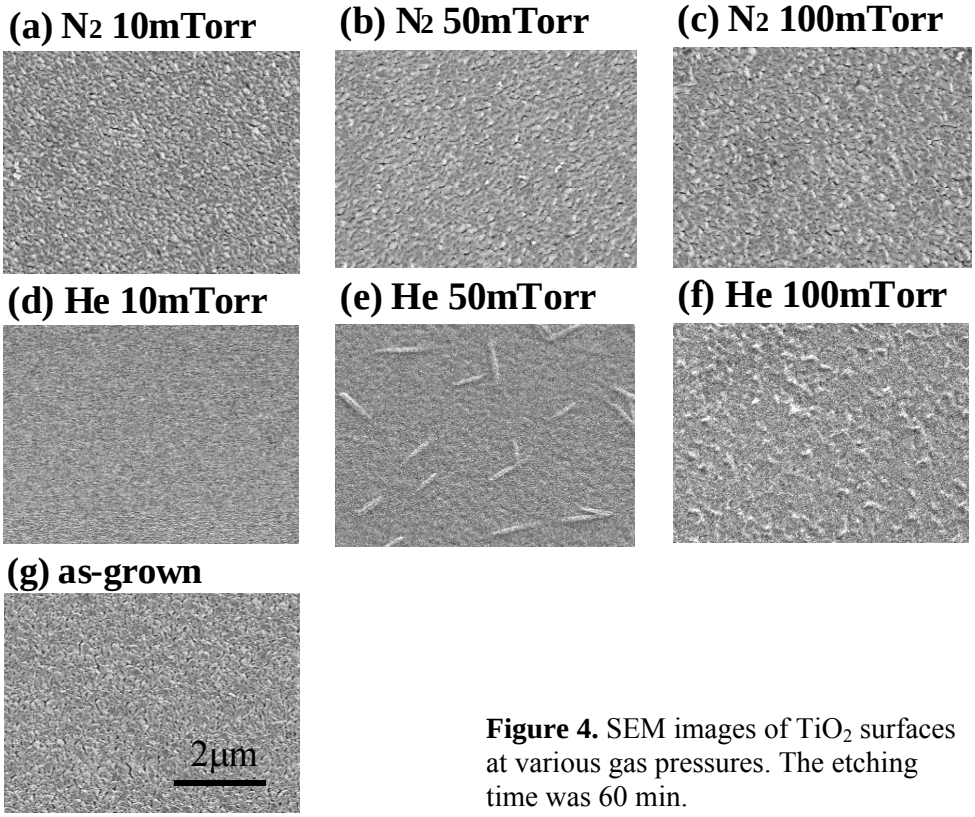

Figure 4. SEM images of TiO_2 surfaces at various gas pressures. The etching time was 60 min.

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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