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# Characteristics of $TiO_2$ thin films surfaces treated by $O_2$ plasma in dielectric barrier discharge with the assistance of external heating

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ABSTRACT

$TiO_2$ thin films were treated with plasma with the assistance of external heating. This plasma was produced with an $O_2$ dielectric barrier discharge (DBD) at atmospheric and near-atmospheric gas pressures. For comparison, the samples were annealed in $O_2$ gas and also treated with $O_2$ DBD plasma alone. The effects of these treatments on photocatalytic activity were compared by evaluating the photodecomposition of methylene blue dye in aqueous solution. The photocatalytic activity of the heat-assisted plasma-treated sample was the most enhanced among the treatment processes. The net photodecomposition of the heat-assisted plasma-treated sample was slightly higher than or comparable to that of $TiO_2$ anatase-phase nanoparticle powder. The photocatalytic activity enhancement can be attributed to an increase in the effective concentration of photogenerated carriers on the surface. This increase is driven by the synergistic effect between an increase in the depletion layer width and an increase in the optical absorption due to the crystalline transition from the bronze to the anatase phases. This crystalline transition occurred at a lower temperature than the annealing transformation temperature.



## 1. Introduction

Photocatalytic $TiO_2$ thin films are attractive materials for applications in environmental purification and solar energy conversion [1–6]. This attraction originates from the excellent photocatalytic activity and superior chemical stability of $TiO_2$ under light irradiation. Numerous researchers have proposed various techniques for further enhancing the photocatalytic activity [7,8]. Two representative techniques are well-known for it. One is the growth of nanoparticles with well-defined size and high crystallinity [9]. The other is the doping with metallic elements such as gold [10] and non-metallic elements such as carbon [11]. Post-treatment of grown thin films is also important for enhancing their photocatalytic activity. The annealing treatment of $TiO_2$ is a well-known technique to improve the film quality of the bulk, thus enhancing the photocatalytic activity [12,13]. $O_2$ plasma treatment on $TiO_2$ is a simple and efficient technique to improve the film quality of the surface [14], because the number of intrinsic point defects, such as oxygen vacancies, on the surface is larger than in the bulk [15]. However, $O_2$ plasma treatment has a serious problem in the case of high-energy ions impinging on the surface [16]. The impact of high-energy ions introduces a large number of point defects into the surface. Damage-free plasma treatment is desirable for surface treatment processes.

Low-temperature or non-thermal $O_2$ plasma generated at atmospheric and near-atmospheric gas pressures using the dielectric barrier discharge (DBD) method [17,18] is suitable for damage-free plasma treatment on $TiO_2$ thin film surfaces. This stems from the fact that the energy of impinging ions from $O_2$ DBD plasma generated at atmospheric and near-atmospheric gas pressures is low enough to suppress the introduction of point defects into the surface, as compared to that of impinging ions from $O_2$ plasma generated at low gas pressure, such as 10 Pa [19]. However, we consider that only the $O_2$ DBD plasma treatment on $TiO_2$ is insufficient for further enhancing the photocatalytic activity because it

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only contributes to the improvement of the film quality of the surface. We propose performing $O_2$ DBD plasma treatment on $TiO_2$ with the assistance of an annealing in the present study. The assistance of an annealing is thought not only to improve the film quality of the bulk but also to vigorously activate reactions between the plasma and the surface and adequately remove point defects introduced by the plasma treatment into the surface. To the best of our knowledge, there have been few reports on $TiO_2$ thin film surfaces treated by $O_2$ DBD plasma treatment with the assistance of external heating. Hereafter, for the sake of simplicity, $O_2$ DBD plasma treatment with the assistance of external heating is simply referred to as heat-assisted plasma treatment (Table 1). Clarifying the characteristics of $TiO_2$ thin film surfaces induced by heat-assisted plasma treatment is important for more effectively enhancing the photocatalytic activity.

In the present study, we investigate the effects of heat-assisted plasma treatment on $TiO_2$ thin film surfaces by employing a homemade DBD reactor [20] with a heat unit. In particular, we focus on the heat-assisted plasma treatment effect on the photocatalytic activity of $TiO_2$ thin films. For evaluation of the photocatalytic activity, we analysed the photodecomposition of methylene blue (MB) dye [21] in aqueous solution. For comparison, the samples were annealed in $O_2$ gas under the same condition and in the same reactor as used for heat-assisted plasma treatment (Table 1). The samples were also treated only with $O_2$ DBD plasma generated without a heat unit. Hereafter, for the sake of simplicity, $O_2$ DBD plasma generated without a heat unit or without the assistance of external heating is simply referred to as plasma only (Table 1). The comparison between the surface characteristics induced by these three treatment processes is beneficial for deeper understanding of the effect of heat-assisted plasma treatment. We discuss the photocatalytic activities of the treated samples predominantly in terms of the crystallisation behaviour and a compositional change in the surface.

## 2. Experiment

In order to treat $TiO_2$ samples with heat-assisted plasma, we employed a homemade DBD plasma reactor [20] equipped with a heat unit (Hakko DG2N-100), as shown in Fig. 1. The type of gas used was $O_2$ gas with a purity of 99.9 vol %. The heat-assisted plasma treatment was performed for 60 min at $O_2$ gas pressures of 100, 10, and 1 kPa while maintaining the sample stage at a constant temperature of 300 °C. The rate of gas flow at the sample stage was held constant at 15 ml/min. The distance between two electrodes was 2 mm. These two electrodes were 40 mm in diameter. One of the two electrodes made of SUS316 stainless steel was electrically grounded and connected to the heat unit. The heat unit controlled the temperature measured by a thermocouple placed in the sample stage. Samples $12.5 \times 12.5$ mm$^2$ in size were placed on the surface of this electrode, i.e., the sample stage. The temperature of the sample stage was maintained at 300 °C by the heat unit during the heat-assisted plasma treatment. The other electrode was covered with a dielectric barrier, 50 mm in diameter and 1 mm in thickness, made of alumina (Nikkato SSA-T). This electrode was connected to a sinusoidal power source at a frequency of 25 kHz

**Table 1**
Three treatment processes applied to $TiO_2$ thin films

| Process | Power source | Heat unit |
|---|---|---|
| Gas annealing | off | on |
| Plasma only | on | off |
| Heat-assisted plasma | on | on |

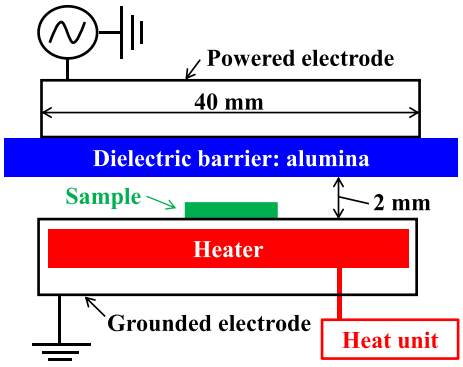


**Fig. 1.** Schematic drawing of DBD plasma reactor equipped with a heat unit. Heat-assisted plasma treatment was performed by turning on the power of the heat unit. Gas annealing was performed without generating plasma. Plasma-only treatment was performed by turning off the power of the heat unit.

(Tamaoki Electronics, TE-HVS300-1425-C). The peak value of the voltage applied to the electrode was set to be comparable to that of the breakdown voltage of the discharge in order to suppress plasma-induced damage on the samples. The root mean square (RMS) value of the applied voltage or the breakdown voltage decreased from 1 to 0.3 kV as the gas pressure decreased from 100 to 1 kPa (Table 2). The RMS value of the discharge current decreased from 10 to 3 mA upon decreasing gas pressure from 100 to 1 kPa, and the average value of the power consumption also decreased from 10 to 1 W (Table 2).

For comparison, the samples were annealed for 60 min in $O_2$ gas at a constant temperature of 300 °C by changing the gas pressure between 100 and 1 kPa in the same reactor. The rate of gas flow at the sample stage was held constant at 15 ml/min, as in the case of heat-assisted plasma treatment. The samples were also treated for 60 min with the plasma only. The gas pressure was varied between 100 and 1 kPa, while the gas flow rate was kept at 15 ml/min, as in the case of heat-assisted plasma treatment. The breakdown voltage of the discharge or the applied voltage, the discharge current, and the power consumption measured in the plasma only were almost the same as those in the heat-assisted plasma. The temperatures of the sample stage during the plasma-only treatments at 100, 10, and 1 kPa increased from the room temperature to 70, 58, and 30 °C, respectively.

The specimens used were $TiO_2$ thin films grown on unheated glass, $50 \times 50$ mm$^2$ in area, by direct current (DC) facing-target sputtering (FTS) [22–24]. The specimens were cut into small pieces for the samples. The thickness of the grown thin films was $448 \pm 77$ nm, as measured using ultraviolet (UV)-visible spectrophotometry (Hitachi U-3900). The grown thin films exhibited the bronze phase [25–28], as measured using X-ray diffraction (XRD, Rigaku RINT-2200/PC). The XRD patterns of the treated samples were determined with the same measuring instrument as that used for the as-grown sample. The optical absorption coefficients of treated samples were measured using UV–visible absorption spectroscopy (Hitachi U-3900). The chemical compositions of treated surfaces were analysed via X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000).

For evaluation of the photocatalytic activity, photodecomposition of MB dye in deionised water was performed for 12 and 24 h under UV irradiation at wavelengths of 300–400 nm emitted from a blacklight lamp. The sample area used for the photodecomposition was $12.5 \times 12.5$ mm$^2$. The emitted UV had a maximum peak of intensity at a wavelength of 365 nm and an intensity of 1 mW/cm$^2$ at the sample surface. The flux of UV photons impinging on the surface was estimated to be approximately $1.8 \times 10^{19}$ m$^{-2}$s$^{-1}$. The