

Study on Fabrication of Titanium Oxide Films by Oxygen Pressure Controlled Pulsed Laser Deposition

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Titanium oxide films were formed using a titanium target by a pulsed laser deposition (PLD) technique under different oxygen pressures from 10^{-6} to 100 Pa. Their densities and thickness were evaluated from total external X-ray reflection profiles and their atomic structures were determined by grazing incidence X-ray scattering (GIXS), and their surface morphology was observed by atomic force microscopy (AFM). The atomic structures of the films were gradually changed from metal titanium through TiO to Rutile-type titanium dioxide TiO₂. The film surfaces became rough above 13.3 Pa oxygen pressure during deposition. Their UV transmission spectroscopy was also observed to predict their photocatalytic activities.

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1. Introduction

Titanium dioxide (TiO₂) is a well-known photocatalyst for decomposition of H₂O to form H₂ and O₂ with UV irradiation.¹⁾ At present, TiO₂ powder is mainly used because of its good photocatalytic activity. On the other hand, thin films as a catalyst form have been required in the application of photocatalysts for photodecomposition of water, since they can be easily separated from the reactant suspension. Thus, many works on TiO₂ films have been made. Photocatalytic activity of the film is, however, still inferior to that of the powder. In the present study, Titanium oxide films are prepared at different oxygen pressures by pulsed laser deposition (PLD) using a Ti metal target. Their structures and surface roughness were investigated by X-ray diffraction and atomic force microscope (AFM). The present work is a part of our series of studies to fabricate a TiO₂ film with better photocatalytic activity.

There are numerous studies on TiO₂ films produced by various methods, such as DC reactive magnetron sputtering,²⁻⁴⁾ RF sputtering,⁵⁾ RF magnetron sputtering,⁶⁻⁸⁾ atomic layer deposition,⁹⁾ etc. In the present study, we employed PLD because this method enables us not only to comparatively easily grow a sub-micron thick film that has the same composition as that of target materials, but also to have many choices of target materials and ambient gas during deposition in a wide range of pressures. This allows us to design different types of films with various structures. Recently, there are many works on fabrication of TiO₂ films by PLD.¹⁰⁻²¹⁾ There are, however, few works on PLD to utilize a chemical reaction between deposited materials and ambient gas during deposition. In the present work, we prepared titanium oxide films by oxidizing titanium metal during PLD in a certain oxygen pressures from 10^{-6} to 10^{-2} Pa. Their atomic structures and mass densities were determined by a grazing incidence X-ray scattering (GIXS) technique and

their surface roughness was investigated by atomic force microscopy (AFM). The features of the films grown in different oxygen pressures will be systematically investigated. Their UV-visible transmittance spectra were also measured to evaluate their photocatalytic activities.

2. Experimental

A pure titanium target with 10 mm diameter and 2 mm thickness was prepared by pelletizing pure titanium powder (>99.9%) with a uniaxial press at 20 MPa, followed by sintering for 14.4 ks at 1273 K in an argon atmosphere. Films were deposited by PLD on quartz glass substrates parallel to and 65 mm apart from the target. A pulsed Nd:YAG laser ($\lambda = 1064$ nm) with 400 mJ and 50 Hz was irradiated to the target for 6 s in a direction of 60° from outside of a reaction chamber through a sapphire window. The appearance of the present PLD apparatus is schematically shown in Fig. 1.

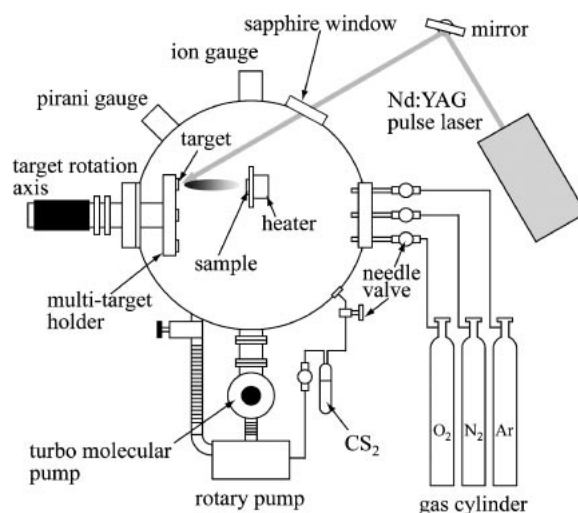


Fig. 1 Schematic diagram of atmosphere-controlled pulsed laser deposition (ACPLD) apparatus.

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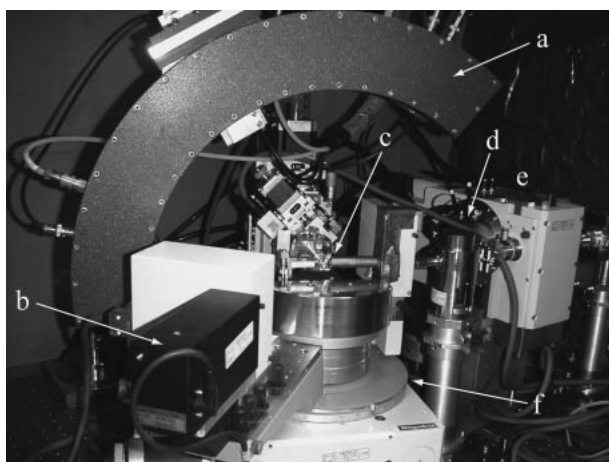


Fig. 2 X-ray apparatus developed for measurements of grazing incidence X-ray scattering (GIXS) and reflectivity from a film sample. In the figure, a is a curved position sensitive proportional detector for GIXS measurements, b a scintillation counter for reflectivity measurements, c a film sample, d Ge 111 monochromator and e X-ray generator.

After the reaction chamber was evacuated at about 1.0×10^{-6} Pa, oxygen gas was introduced and then the chamber was kept airtight during deposition. Oxygen gas pressure during deposition was varied from 1.0×10^{-4} to 113 Pa.

Surface roughness of the deposited films was observed by AFM (Shimadzu SPM 9500J2). The film densities and thicknesses were determined from critical angles and periods of oscillations of X-ray reflectivity curves.²²⁾ For investigation of the film structures, the grazing incidence X-ray scattering (GIXS) method²³⁾ was employed in order to observe scattering intensities from the films of about 10 nm thickness without an extremely large contribution from a quartz glass substrate. All these measurements were carried out with Cu $K\alpha$ radiations generated at 50 kV and 250 mA with a Ge 111 incident monochromator. The apparatus designed for X-ray reflectivity and GIXS measurements is shown in Fig. 2. Absorption spectra of the films were obtained by a UV-visible spectroscopy system (Shimadzu, UV-2550) equipped with an integral sphere (Shimadzu, ISR-2200).

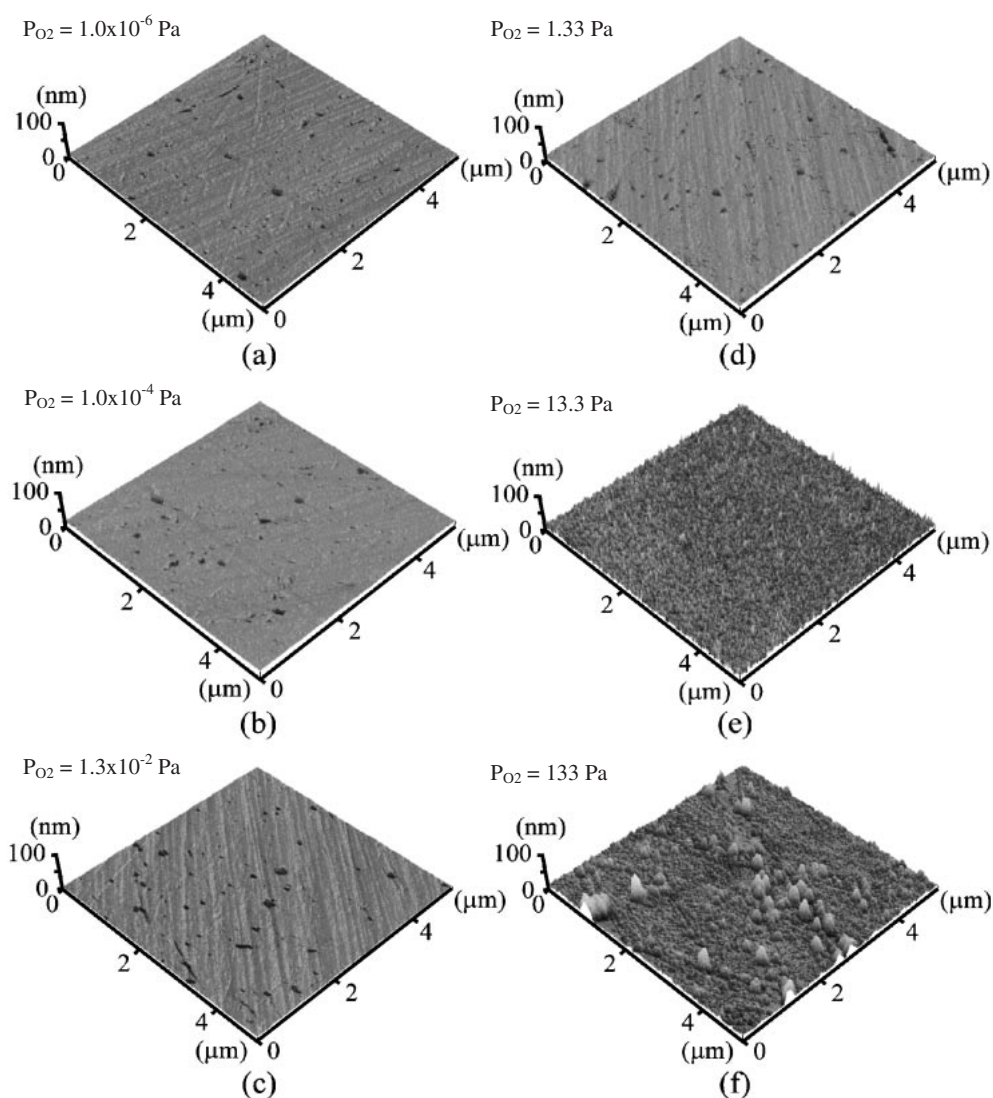


Fig. 3 Atomic force microscope images of films deposited by PLD at (a) 1.0×10^{-6} PaO₂, (b) 1.0×10^{-4} PaO₂, (c) 1.3×10^{-2} PaO₂, (d) 1.33 PaO₂, (e) 13.3 PaO₂ and (f) 133 PaO₂.

3. Results

AFM images of the as-deposited films are shown in Fig. 3. Surfaces of the films deposited below an oxygen pressure of 1.33 Pa (hereafter, it will be described as 1.33 PaO₂) are relatively smooth, and there is no significant difference in appearance. Among the films, many small particles are present in the film deposited at 13.3 PaO₂ and they grow larger up to about 0.1 μ m in diameter at 133 PaO₂.

X-ray reflectivities of the films and the quartz glass substrate are compared in Fig. 4. Critical angles for the total external reflections are defined as the inflection points indicated by arrows in Fig. 4. Film densities were calculated from these critical angles. Thicknesses of the films are evaluated from the periods of oscillations above the critical angles. The densities and thicknesses are summarized in Table 1. The thicknesses are about 14 nm, independent of the oxygen pressure below 1.33 Pa while the densities show the maximum at 1.3×10^{-2} PaO₂. The reflection profiles were

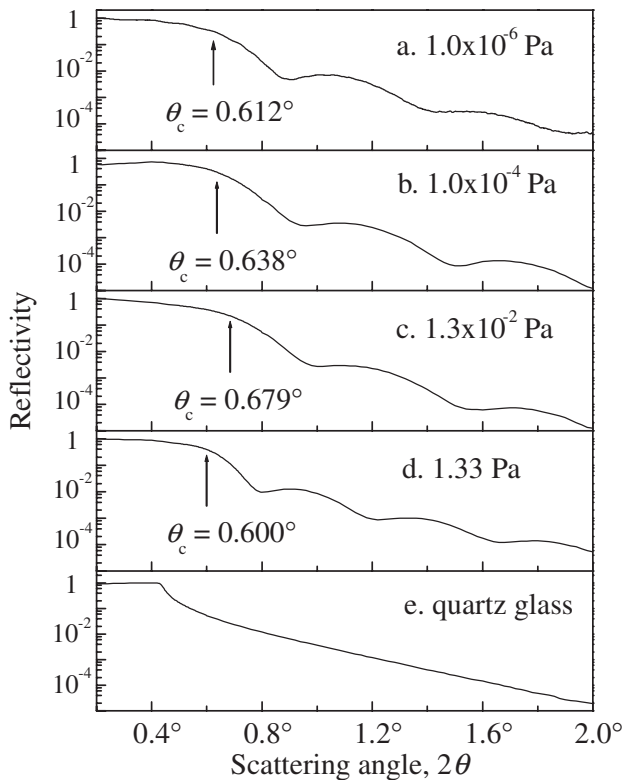


Fig. 4 X-ray reflectivity profiles of the films deposited by PLD at (a) 1.0×10^{-6} PaO₂, (b) 1.0×10^{-4} PaO₂, (c) 1.3×10^{-2} PaO₂ and (d) 1.33 PaO₂, and (e) a quartz glass substrate.

Table 1 Densities and thicknesses of the films prepared by PLD at different oxygen pressures. They are evaluated from critical angles and periods of oscillations of X-ray reflectivity profiles in Fig. 4.

Oxygen pressure (PaO ₂)	Density (Mg/m ³)	Thickness (nm)
1.33×10^{-6}	4.7 ± 0.1	14 ± 1
1.33×10^{-4}	5.2 ± 0.1	13 ± 1
1.33×10^{-2}	5.8 ± 0.1	13 ± 1
1.33	4.4 ± 0.1	17 ± 1

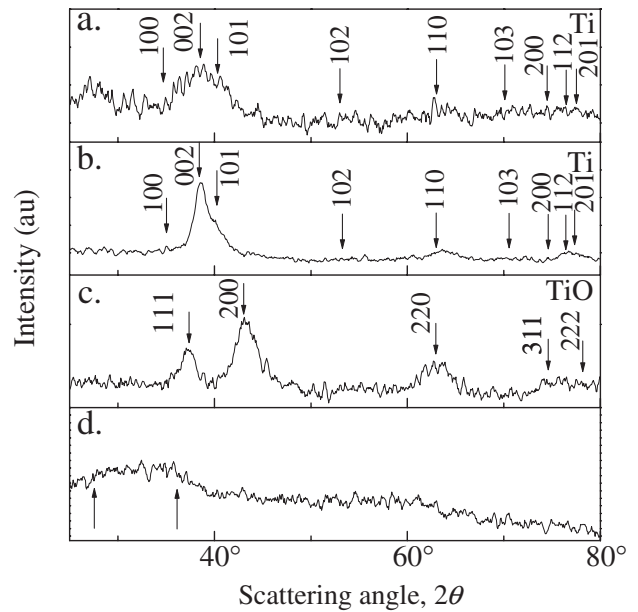


Fig. 5 Grazing incidence X-ray scattering (GIXS) profiles of the films deposited by PLD at (a) 1.0×10^{-6} PaO₂, (b) 1.0×10^{-4} PaO₂, (c) 1.3×10^{-2} PaO₂ and (d) 1.33 PaO₂.

not obtained from the films deposited at 13.3 and 133 PaO₂ because of their surface roughness due to the small particles shown in the AFM images of Figs. 3(e) and (f).

The color of the films changes with the oxygen pressure. Without introducing oxygen gas to the chamber, *i.e.* 1.0×10^{-6} Pa, the film shows metallic silver. With increase in oxygen gas pressure, the color of the plume changes from blue to white. Dark blue color films were formed when the oxygen pressures are 1.0×10^{-4} , 1.3×10^{-2} and 1.33 Pa. On the other hand, the films become transparent, prepared at 13.3 and 133 PaO₂.

Grazing incident angle are set just above the critical angle so that quite large scattering intensity from the film is obtained, being kept in relatively small contribution from the substrate. GIXS profiles of the films are shown in Fig. 5. From the result that the density calculated from the critical angle of the film deposited at 1.0×10^{-6} PaO₂, 4.7 ± 0.1 Mg/m³, is close to the density of pure titanium (4.54 Mg/m³) and a broad peak at about 40° coincides with the titanium 002 and 101 peaks, we consider that the deposited film is titanium. Slight increase in the density may, however, indicate that it is insignificantly oxidized during the deposition. Diffraction peaks of the film deposited at 1.0×10^{-4} PaO₂ are attributed to titanium as it is shown in Fig. 5(b) although the film density is 5.2 Mg/m³. Thus, oxidation proceeds in the film. In the film deposited at 1.3×10^{-2} PaO₂, broad peaks ascribed to titanium oxide TiO are observed. Its density coincides with that of TiO (5.82 Mg/m³). By increase in the partial oxygen pressure during the deposition, no clear diffraction peaks are observed; only a broad hump is present at about 32°. Since there are two strong Rutile 110 and 101 peaks at 27.4° and 36.1° indicated with the arrows in Fig. 5(d) and the film density 4.4 ± 0.1 Mg/m³ is close to that of Rutile phase (4.23 Mg/m³), the film is considered to be Rutile-type TiO₂ phase. In order to confirm

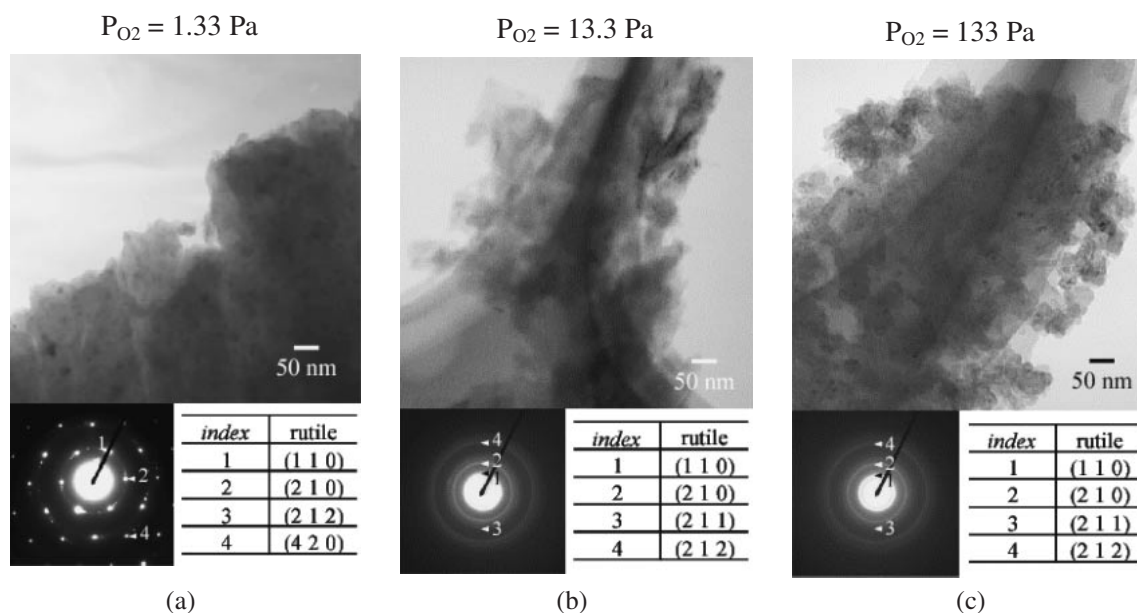


Fig. 6 Electron transmission micrographs of the films deposited at (a) 1.33 PaO₂, (b) 13.3 PaO₂ and (c) 133 PaO₂.

this result, we observed this film with a transmission electron microscope.

In Fig. 6(a), bright field image and electron diffraction pattern are shown. From the electron diffraction, we find that the film is the Rutile-type TiO₂ phase. The electron microscopy observation was also carried out in the films of Figs. 3(e) and (f), prepared at 13.3 and 133 PaO₂. Because of their rough surface, the GIXS measurements could not apply to these films. As is seen in electron diffraction patterns of Figs. 6(b) and (c), both films are also the Rutile-type TiO₂ phase. Therefore, by setting an appropriate oxygen gas pressure from 1.0×10^{-6} to 133 Pa during PLD, the structure of the film is controlled to titanium, titanium oxide TiO or Rutile-type titanium oxide TiO₂.

4. Discussion

Photocatalytic activity is the important concern about titanium oxide films. In order to predict photocatalytic activities of the films prepared in the present work, UV transmittance spectra of the films were measured. The spectra of the films prepared at the different oxygen pressures are compared in Fig. 7. Naturally, the transmittance spectra of the films deposited at 1.0×10^{-6} and 1.0×10^{-4} PaO₂ in Figs. 7(e) and (f) have no absorption edge since they are basically titanium metallic films as is shown GIXS profiles in Figs. 5(a) and (b). Accompanied with increase in oxygen pressure during PLD, oxidation of titanium progressed. A photo-absorption edge appears around 300 nm and the films gradually become transparent for visible lights. As is explained in Fig. 5(c), the film deposited at 1.3×10^{-2} PaO₂ is titanium oxide TiO. Although TiO has no photo-absorption in the range from 240 to 600 nm from our UV-visible spectroscopy measurement with its powder, a slight increase of the transmittance around 300 nm is observed. This wavelength almost coincides with those of the absorption edges of the films prepared at higher oxygen pressures above

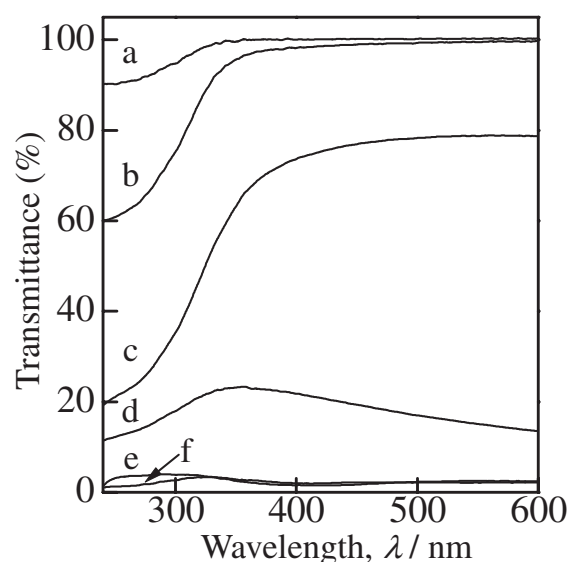


Fig. 7 Transmittance spectra of the films prepared at different oxygen partial pressures by PLD. The oxygen pressures are (a) 1.0×10^{-6} Pa, (b) 1.0×10^{-4} Pa, (c) 1.3×10^{-2} Pa, (d) 1.33 Pa, (e) 13.3 Pa and (f) 133 Pa.

1.3×10^{-2} Pa. We have already known that these films are the Rutile-type TiO₂ phase. Thus, even in the film prepared at 1.3×10^{-2} PaO₂, the Rutile-type TiO₂ phase may be partially grown. On the other hand, the absorption edge of the Rutile-type TiO₂ phase is 413 nm.²⁴⁾ The difference in the wavelength between the present Rutile-type TiO₂ film and the reported value probably arises from very fine crystalline sizes²⁵⁾ as we observed in the X-ray diffraction profile of Fig. 5(d) and the transmission electron micrographs of Fig. 6.

In the Rutile-type TiO₂ films prepared at the oxygen pressures above 1.33 Pa, the absorption edge appears at about 300 nm. As long as the photo-catalytic activity is judged from the position of the absorption edge in the transmittance spectra, a good photocatalytic activity is not expected in the

present oxide films in comparison with the powder TiO₂. However, feasibility of the atmosphere-controlled pulsed laser deposition (ACPLD) technique for producing titanium compound films has been successfully demonstrated in the present work. The advantage of the present method is that elements in atmosphere gas with a couple of % to dozens % can be added to the films, using a reaction between the gas and the target materials during deposition. In other words, a comparatively large amount of elements, such as sulfur, nitrogen, *etc.* can be added by this ACPLD method in comparison with the other film preparation techniques. This may be important to drastically improve the photocatalytic activity of titanium oxide films.

5. Summary

Titanium oxide films were prepared by the ACPLD method. The film structures become titanium, TiO or Rutile-type TiO₂ depending on the oxygen during deposition between 1.0×10^{-6} Pa to 133 Pa. Very fine crystalline structures in the Rutile-type TiO₂ films cause the absorption edge to be shift to a shorter wavelength. Thus, the present Rutile-type TiO₂ film on its own may not be expected to show a good photocatalytic activity in comparison with the titanium oxide TiO₂ powder. It is, however, clearly demonstrated that the ACPLD method itself is especially useful to prepare a film containing a large amount of additional elements.

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