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Preparation of TiO_2 by a nearby vaporization chemical vapor deposition method

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Titanium dioxide (TiO_2) is widely used for decomposition of organic molecules [1], and decomposition of H_2O [2] based on its photo catalytic activity, besides antireflection coatings for optical devices [3] and film coatings for dye-sensitized solar cells [4, 5]. Because of a high photocatalytic activity, anatase crystalline of TiO_2 has been widely applied to many fields such as environmental purification [6], and medical treatment [7].

Different deposition techniques for the growth of TiO_2 have been reported by many researchers. Out of the many deposition techniques, chemical vapor deposition method using metal organic compounds as precursors (MOCVD) has the advantage of low-cost and convenience since this technique is a low temperature process. However, the usual MOCVD deposition apparatus becomes complicated because a carrier gas is used and furthermore, the gas has to be heated.

The present report concerns the formation of TiO_2 films by a new modification of CVD method, in which vaporization takes place by radiant heat from the substrate without carrier gas. This deposition technique named "nearby vaporizing CVD (NV-CVD)" has several advantages: low cost, energy saving, and easy control with few experimental parameters. Since no carrier gas is used, the present experimental set-up is regarded as the simplest CVD apparatus available to date.

The schematic diagram of an apparatus and preparation conditions are shown in Fig. 1. Using this apparatus of NV-CVD under atmospheric pressure, TiO_2 films were prepared on the experimental condition listed in Table I. The substrate was heated by a hot Al suscepter with a resistance cartridge heater. The substrate temperature was sensed by a thermocouple inside the Al suscepter. Tetra isopropyl titanate, $[(CH_3)_2CHO]_4Ti$, was used as a source material. In order to control the intensity of radiant heat from the nearby substrate, distance (D) between the substrate and the surface of source material was adjusted using a micrometer. The thickness and refractive index of the films deposited on Si(100) substrate were measured by an elipsometer (Mizojiri Optical DVA-36L) with a light beam at 632.8 nm. The deposition rate was calculated from the thickness and the time for the film grown to ca. 50 nm. The surface morphology was observed using a scanning electron microscope (SEM; Jeol-5310LVB) for the films deposited on a fused quartz plate.

TABLE I Preparation conditions

Source material	Tetra isopropyl titanate $\{[(CH_3)_2CHO]_4Ti\}$ (TTIP)
Substrate	Si(100) and fused quart
Vessel of source material	PTFE (polytetrafluoroethylene), Al
Substrate temperature (T_s)	300–600 °C
Distance between the substrate surface and the surface of the source material (D)	2.5–10 mm

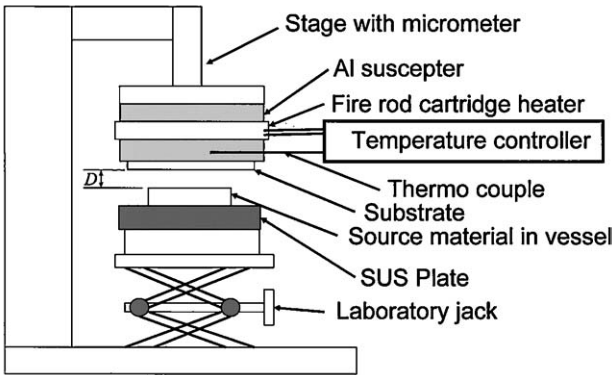


Figure 1 Schematic view of nearby vaporizing CVD apparatus.

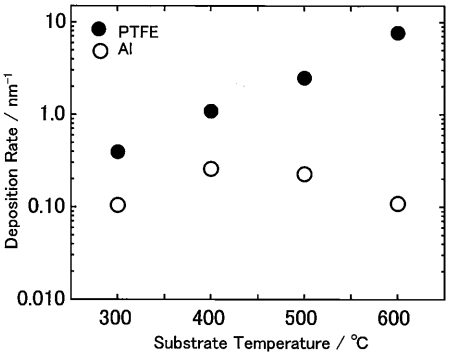


Figure 2 Relationship between the substrate temperature and the rate of TiO_2 film deposition at $D = 5.0$ mm.

Fig. 2 shows the relationship between the deposition rate of TiO_2 films and the temperature of Si(100) substrate. In the case of using PTFE as a vessel of the source material, the deposition rate increases exponentially from 0.13 to 8 nm s^{-1} with the substrate temperature. The exponential increase of the deposition rate results from the exponential increase in vapor pressure of the source material with the substrate temperature. On the other hand, when an aluminum vessel was used in place of PTFE, the deposition rate increased with increasing the substrate temperature to a certain point

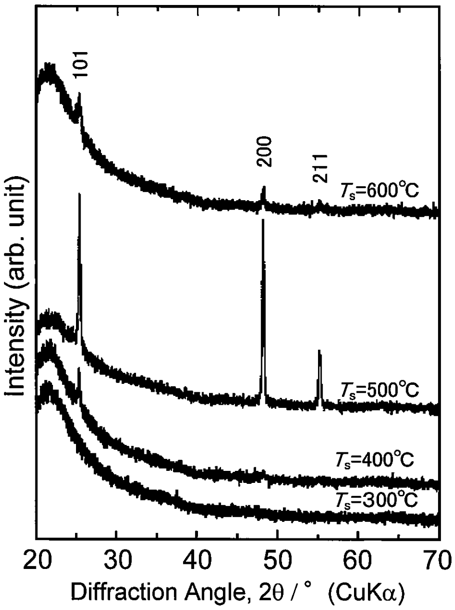
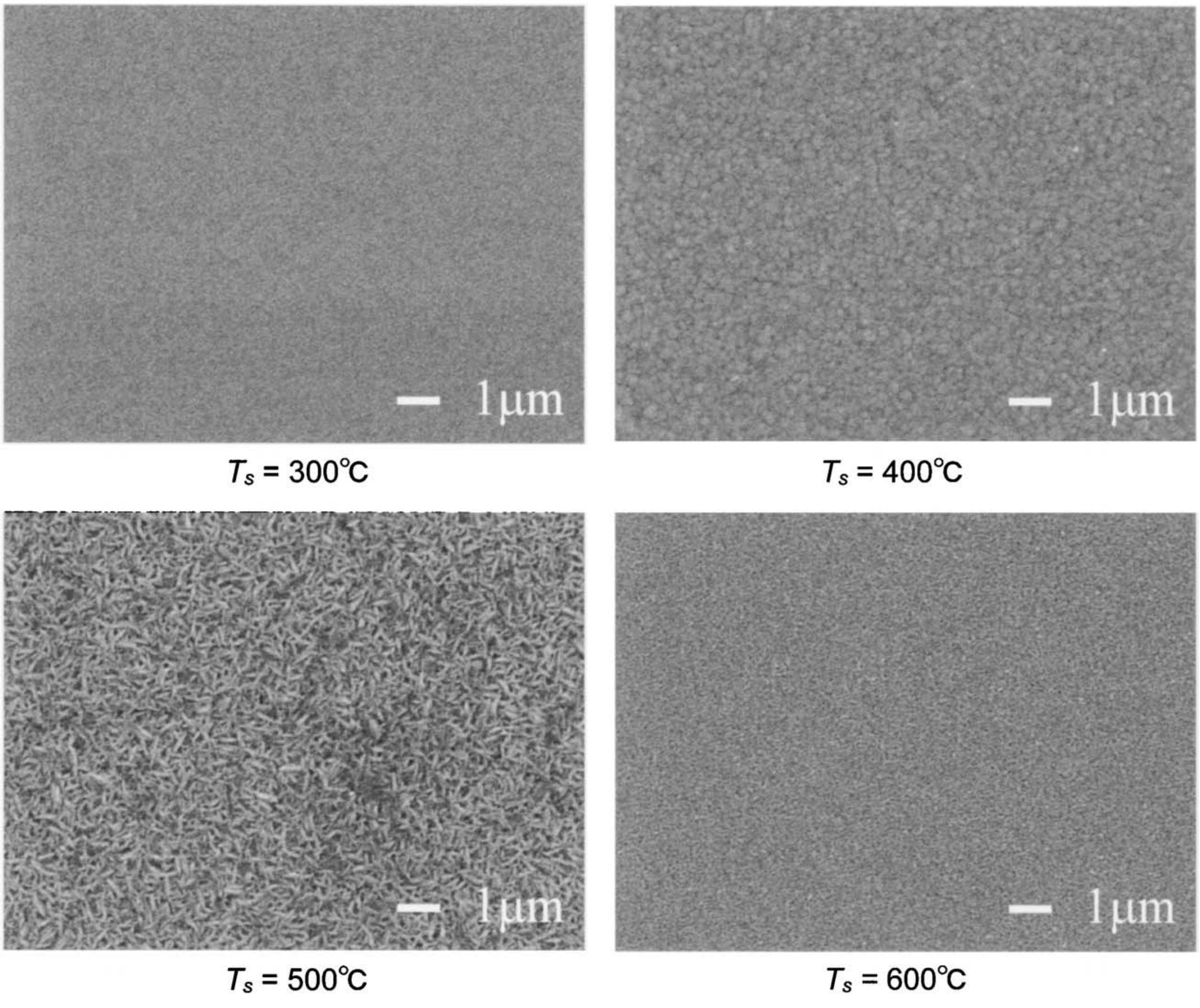


Figure 3 XRD patterns of the TiO_2 films obtained with a PTFE vessel at various substrate temperatures, T_s, under the condition of $D = 5.0$ mm.

but it decreased at a higher temperature. This difference in the temperature dependence is explained by the difference in the temperature of the source material due to different heat conductivities of the vessels. The increase of the temperature of source material by radiant heat is obstructed by the higher heat conductivity of Al metal. At a higher substrate temperature, the surface reaction becomes rapid. However, the vapor pressure of the source material in Al vessel is low enough for the deposition rate to be controlled by mass transfer and furthermore, the nucleation takes place at homogenous gas phase [8]. On the other hand, in the case of using PTFE vessel, since the vapor pressure of the source material is higher than that while using Al vessel, mass transfer is not the rate-controlling step and there is no substantial decline in the deposition rate at the higher temperature. The possible increase in the nucleation process at homogenous gas phase may be negligible when using a PTFE vessel.

Fig. 3 shows the X-ray diffraction patterns of the TiO_2 films deposited at various substrate temperatures ranging from 300 to 600 °C and at substrate distance $D = 5.0$ mm. The best crystallinity of the TiO_2 was obtained at $T_s = 500$ °C. Furthermore, at this temperature a preferred orientation to $\langle 100 \rangle$ and $\langle 101 \rangle$ of the TiO_2 films became remarkably strong. An amorphous or low crystallinity property of the deposited films obtained at low substrate temperatures might result from a lack of the thermal energy for crystallization at the surface. The decreased crystallinity of the film prepared at $T_s = 600$ °C may be caused by the vigorous reactions



T_s = 300°C

T_s = 400°C

T_s = 500°C

T_s = 600°C

Figure 4 SEM photographs of TiO_2 films obtained at various substrate temperatures, T_s under the condition of $D = 5.0$ mm with a PTFE vessel.

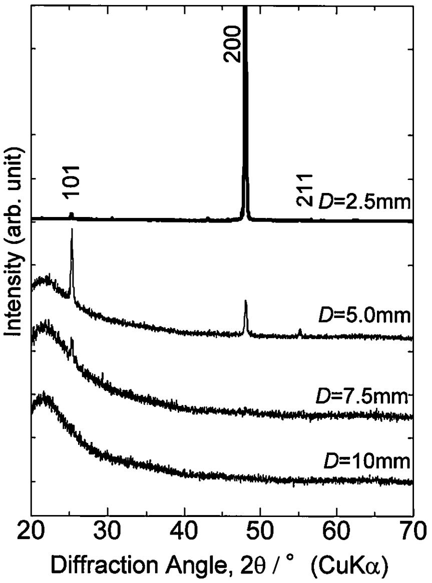


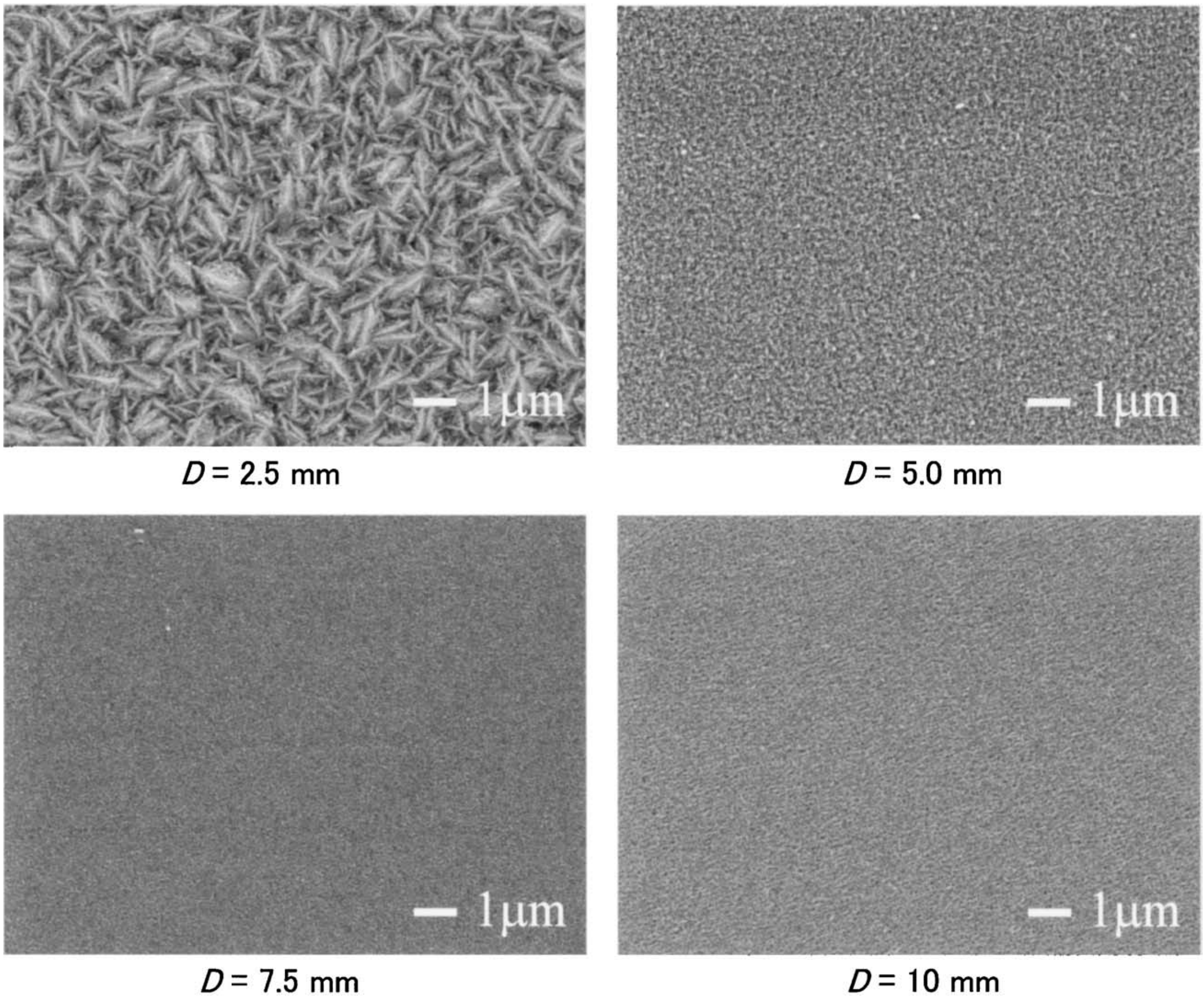
Figure 5 XRD patterns for the TiO_2 films prepared at various distances, D, under the condition of $T_s = 550\,^\circ C$ with a PTFE vessel.

of the source material. Namely, a rapid increase in the nucleation rate results in the formation of the small size crystallites.

Fig. 4 shows SEM photographs of the TiO_2 films obtained at $D = 5.0$ mm and $T_s = 300$, 400, 500 and 600 °C. At each temperature the obtained film changes its structure: smooth amorphous-like surfaces (300 °C), granular (400 °C), cloth-like texture (500 °C), and cloth-like fine texture (600 °C). These surfaces morphologies correspond to the observed XRD patterns in Fig. 3.

Fig. 5 shows the X-ray diffraction patterns of the TiO_2 films deposited at various substrate source distances at $T_s = 550\,^\circ C$. A $\langle 100 \rangle$ preferred orientation of anatase TiO_2 film was obtained at $D = 2.5$ mm. A $\langle 100 \rangle$ and $\langle 101 \rangle$ orientation was observed at $D = 5.0$ mm, $\langle 101 \rangle$ orientation at $D = 7.5$ mm, and an amorphous phase at $D = 10$ mm. As far as we know, a strong $\langle 100 \rangle$ preferred orientation of anatase TiO_2 has not been commonly reported. Usually in the CVD method with this source material, 101 and 211 diffraction peaks are accompanied with $\langle 100 \rangle$ preferred orientation and this orientation becomes strong only at a higher substrate temperature [9]. Since the present CVD apparatus needs no carrier gas, the temperature to produce the $\langle 100 \rangle$ preferred orientation could be decreased.

Fig. 6 shows SEM photographs of the TiO_2 films obtained at the distance D ranging from 2.5 to 10 mm and $T_s = 550\,^\circ C$. The films grown at $D = 2.5$ mm had surfaces with cloth-like coarse texture structure, and granular structure at $D = 5.0$ mm, while the films deposited at $D = 7.5$ mm and 10 mm had smooth



D = 2.5 mm

D = 5.0 mm

D = 7.5 mm

D = 10 mm

Figure 6 SEM photographs of TiO_2 films obtained at various distances, D under the condition of $T_s = 550\,^\circ C$ with a PTFE vessel.

featureless surfaces. These surface morphologies observed by SEM are consistent with the XRD patterns in Fig. 5.

In conclusion, TiO_2 films were very simply prepared by NV-CVD under atmospheric pressure using tetra isopropyl titanate in the absence of carrier gas. The heat conductivity of the vessel of source materials affected the deposition modes. The important results obtained in the present study are the following: (i) the deposition rate increases exponentially from 0.13 nm min^{-1} to 8 nm min^{-1} with increasing the substrate temperature when PTFE vessel was used, and (ii) strong $\langle 100 \rangle$ preferred orientation of anatase TiO_2 film was obtained at $D = 2.5$ mm and $T_s = 550\,^\circ\text{C}$.

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