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Incubation Time Free CVD-TiO_2 Film Preparation Using a Novel Titanium Precursor, Ti-DOT

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Titanium oxide thin films were deposited at 200 - 400 ℃ on amorphous SiO_2 substrates by chemical vapor deposition (CVD) using novel precursors, diisopropoxo{ethene-1,2-diylbis(*tert*-butylamido)}titanium [Ti[N(^{t}Bu)CH=CHN(^{t}Bu)](O^{i}Pr)$_2$, **1**; Ti-DOT] and di-*tert*-pentyloxo{ethene-1,2-diylbis(*tert*-butylamido)}titanium [Ti[N(^{t}Bu)CH=CHN(^{t}Bu)](O^{t}Pe)$_2$, **2**], with oxygen gas as an oxidant. The deposition amounts of TiO_2 thin films using Ti-DOT and **2** were clearly larger than that of titanium tetraisopropoxide [Ti(O^{i}Pr)$_4$, **3**; TTIP] because of the shorter incubation time in the case of Ti-DOT and **2**. Details of the TiO_2 films from Ti-DOT and TTIP were evaluated by AFM. Compared to the films from TTIP, smaller surface roughness was observed for the films using Ti-DOT. In addition, a TiO_2 thin film deposited from Ti-DOT on an amorphous SiO_2 hole substrate with an aspect ratio of 5 showed good conformability.

1. Introduction

TiO_2 thin films have attracted much attention for a wide range of applications, for instance, antireflection films [1], photocatalysts [2], and biocompatible materials [3], owing to its specific functional properties.

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Among various deposition techniques, atomic layer deposition (ALD) and chemical vapor deposition (CVD) have a great advantage in providing excellent film uniformity and flatness over a large surface area of the substrate. Titanium tetraisopropoxide (TTIP) has been extensively studied as a liquid precursor to prepare TiO_2 thin films by ALD and CVD because of its high vapor pressure, noncorrosive by-products, and the high cost efficiency compared to other metal organic precursors [4-6].

However, other precursors for TiO_2 film preparation have not been widely investigated [7, 8].

In this study, we synthesized novel precursors, diisopropoxo{ethene-1,2-diylbis(*tert*-butylamido)} titanium [$Ti[N(^tBu)CH{=}CHN(^tBu)](O^iPr)_2$, **1**; Ti-DOT] and di-*tert*-pentyloxo{ethene-1,2-diylbis(*tert*-butylamido)} titanium [$Ti[N(^tBu)CH{=}CHN(^tBu)](O^tPe)_2$, **2**] and evaluated their deposition characteristics to prepare TiO_2 thin films by CVD with oxygen gas as an oxidant [9]. The molecular structures of **1** (Ti-DOT), **2**, and **3** (TTIP) are shown in **Fig. 1**. We also examined the surface flatness and the step coverage of the films from Ti-DOT.

2. Experiment

2.1 Preparations

Preparation of compound **1** (Ti-DOT) and **2** were carried out under argon atmosphere using standard Schlenk tube and vacuum-line techniques. Dehydrated hexane and tetrahydrofuran used in this work were purchased from Kanto Chemical Co., Inc. Benzene-d_6 was distilled from sodium/benzophenone ketyl prior to use. TTIP and *tert*-pentyl alcohol were purchased from Aldrich, and were used as received.

Synthesis of $Ti[N(^tBu)CH{=}CHN(^tBu)](O^iPr)_2$ (1; Ti-DOT).

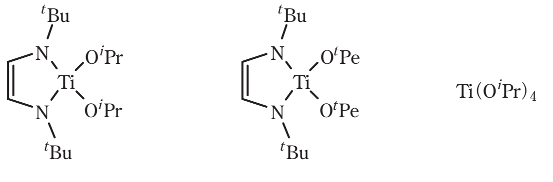
N,N-di-*tert*-butyl-1,4-diazabuta-1,3-diene (2.22 g, 13.2 mmol) [10] was dissolved in 20 mL of tetrahydrofuran, and then sodium (606 mg, 26.4 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. The resulting deep-red solution was added dropwise at -70℃ to a solution of $Ti(O^iPr)_4$ (3.56 g, 12.5 mmol) in 10 mL of hexane. The resulting mixture was allowed to warm to room temperature and stirred for 14h. The solvent was removed under reduced pressure, and the residue was extracted in 20 mL of hexane. A crude material was purified by distillation (85℃ / 0.05 Torr) to obtain 3.91 g of Ti-DOT (93% yield) as a dark red oil. ^1H NMR (500 MHz, C_6D_6, 20℃, δ): 5.96 (s, 2 H, NC*H*=C*H*N), 4.0-5.0 (br, 2 H, $OCH(CH_3)_2$), 1.30 (s, 18 H, $NC(CH_3)_3$), 1.1-1.3 (br, 12 H, $OCH(CH_3)_2$). ^{13}C NMR (125 MHz, C_6D_6, 20℃, δ): 102.7 (N*C*H=*C*HN), 74.5 (br, $OCH(CH_3)_2$), 57.6 ($NC(CH_3)_3$), 31.7 ($NC(CH_3)_3$), 27.8 ($OCH(CH_3)_2$). GC/MS (EI) *m/z* 334 (M^+), 319, 291, 275.

Synthesis of $Ti[N(^tBu)CH{=}CHN(^tBu)](O^tPe)_2$ (2).

To a stirred solution of bis(dimethylamido){ethene-1,2-diylbis(*tert*-butylamido)titanium $Ti[N(^tBu)CH{=}CHN(^tBu)](NMe_2)_2$ [11] (1.76 g, 5.78 mmol) in hexane (7 mL), *tert*-pentyl alcohol (1.02 g, 11.6 mmol) was added dropwise at -70℃ during a period of 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed under reduced pressure, and the residue was purified by distillation (97℃ / 0.05 Torr) to obtain 2.11 g of **2** (93% yield) as a dark red oil. ^1H NMR (500 MHz, C_6D_6, 20℃, δ): 5.93 (s, 2 H, NC*H*=C*H*N), 1.55 (br, 4 H, $OC(CH_3)_2CH_2CH_3$), 1.30 (s, 18 H, $NC(CH_3)_3$), 1.1-1.4 (br, 12 H, $OC(CH_3)_2CH_2CH_3$), 0.99 (br, 6 H, $OC(CH_3)_2CH_2CH_3$). ^{13}C NMR (125 MHz, C_6D_6, 20℃, δ): 103.1 (N*C*H=*C*HN), 81.4 (br, $OC(CH_3)_2CH_2CH_3$), 57.4 ($NC(CH_3)_3$), 38.3 ($OC(CH_3)_2CH_2CH_3$), 31.9 ($NC(CH_3)_3$), 31.1 ($OC(CH_3)_2CH_2CH_3$), 9.8 ($OC(CH_3)_2CH_2CH_3$).

2.2 Deposition of TiO_2 thin films

TiO_2 thin films were deposited on amorphous SiO_2 prepared on n-type Si substrates at the deposition temperature range from 200 to 400℃ by CVD using Ti-DOT, **2**, and TTIP. The vapor of the precursors was generated by bubbling method with a vapor pressure of 91 Pa at 84℃ (Ti-DOT), 111℃ (**2**) and 50℃ (TTIP), respectively. This vaporized precursor was transferred



1 ; Ti-DOT **2** TTIP

Fig. 1 Molecular structures of Ti precursors in this study to the cold wall type CVD reaction chamber with argon carrier gas. The reactant gas was O_2, and its concentration was constantly controlled at 20% of the total reaction chamber pressure. Si wafer covered with 100 nm-thick SiO_2 was used as a substrate. The deposition conditions of TiO_2 thin films are summarized in **Table 1**.

2.3 Measurement of physical properties

Deposition amount of the films was measured by the X-ray fluorescence (XRF) calibrated by standard samples. The crystal structure, film composition, and surface roughness were measured by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM), respectively. The step coverage of the thin film was observed by field emission scanning electron microscopy (FE-SEM).

3. Results and discussions

Fig. 2 shows the relationship between the deposition amounts of TiO_2 films and the inverse of the deposition temperature deposited for 60 min. using Ti-DOT, **2**, and TTIP as a precursor. The deposition characteristics of the three precursors can be divided into two temperature regions. The deposition amounts of TiO_2 films from Ti-DOT, **2**, and TTIP were less sensitive against the deposition temperature above 300℃. On the other hand, strong deposition temperature dependency was observed below this temperature. It is noticeable that the deposition amount of TiO_2 films from Ti-DOT and **2** were several times as large as that from TTIP in each temperature between 250 and 400℃.

The relationship between the deposition amount and the deposition time of TiO_2 films from Ti-DOT, **2**, and TTIP at 300℃ was described in **Fig. 3**. In the case of using Ti-DOT and **2** as a precursor, the incubation time (*time delay for onset of deposition*) is significantly shorter than the case of using TTIP. While TTIP exhibited about 30 min. of incubation time, the incubation time of Ti-DOT was only a few minutes.

Table 1 Deposition conditions of TiO_2 thin films by CVD

Precursor		Ti-DOT	**2**	TTIP
Precursor temperature	[℃]	84	111	50
Carrier gas flow rate	[cm^3/min]		10	
O_2 gas flow rate	[cm^3/min]		60	
Diluent gas flow rate	[cm^3/min]		230	
Total flow rate	[cm^3/min]		300	
Chamber pressure	[Pa]		533	
Substrate temperature	[℃]		200-400	

As shown in **Fig. 2 and 3**, it is indicated that the deposition characteristics of **2** were almost the same as those of Ti-DOT on the condition in **Table 1**. For this reason, further analyses were made only for TiO_2 films from Ti-DOT and TTIP. **Fig. 4** illustrates the average surface roughness, *Ra*, as a function of the deposition amount of the TiO_2 films deposited at 300℃ using Ti-DOT and TTIP. Compared to the *Ra* of the same deposition amount, films from Ti-DOT showed smaller *Ra* than those from TTIP. This indicates that Ti-DOT can deposit films with flatter surface and with shorter incubation time.

Carbon and nitrogen contents of TiO_2 films deposited at 300℃ from Ti-DOT and TTIP were found to be less than 1% from XPS analysis. In addition, these films were ascertained from XRD measurements to be consistent

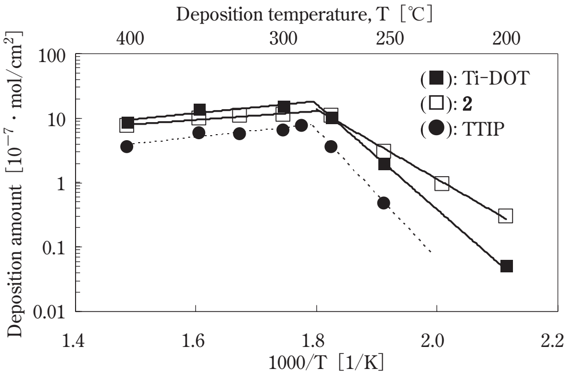


Fig. 2 Deposition temperature dependency of the deposition amount of TiO_2 films deposited for 60 min. using Ti-DOT, **2**, and TTIP

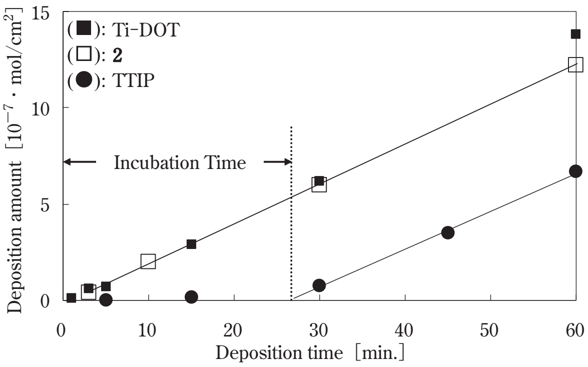


Fig. 3 Deposition time dependency of deposition amount of TiO_2 films deposited at 300 ℃ from Ti-DOT, **2**, and TTIP

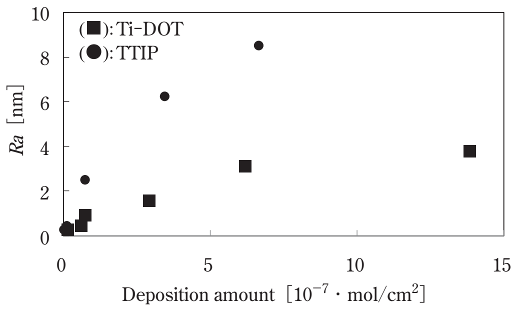


Fig. 4 Deposition amount dependency of average surface roughness, *Ra*, for the TiO_2 films deposited at 300℃ from Ti-DOT and TTIP

with crystalline anatase phase.

Fig. 5 shows a FE-SEM image of a TiO_2 film deposited at 275℃ from Ti-DOT on an amorphous SiO_2 hole prepared on n-type Si substrate with an aspect ratio of 5. The film thickness change from the top to the bottom of the side wall was found to be 95%. Good step coverage without overhang at the upper corner was observed.

4. Conclusions

We have demonstrated here the incubation time free TiO_2 film formation by CVD using novel liquid precursors, Ti-DOT and **2**. TiO_2 thin films were deposited at deposition temperature of 200 – 400℃ by CVD using Ti-DOT, **2**, and TTIP. As compared to TTIP, Ti-DOT and **2** exhibit excellent time efficiency for the formation of TiO_2 thin films, due to shorter incubation time. In addition, the films from Ti-DOT had smoother surface than those from TTIP at 300℃. Furthermore, the film from Ti-DOT deposited at 275℃ showed a good step coverage on a hole substrate. Thus, Ti-DOT is a promising precursor for TiO_2 thin film preparation by CVD.

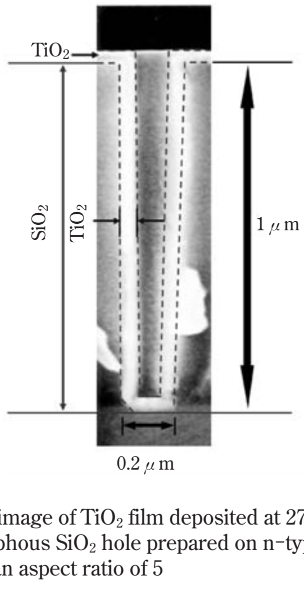


Fig. 5 SEM image of TiO_2 film deposited at 275℃ on an amorphous SiO_2 hole prepared on n-type Si substrate with an aspect ratio of 5

5. References

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