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Preparation of Large Area TiO_2 Thin Films by Low Pressure Chemical Vapor Deposition

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Preparation of Large Area TiO_2 Thin Films by Low Pressure Chemical Vapor Deposition

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Abstract Chemical vapor deposition using titanium tetra-isopropoxide (TTIP) was employed to investigate effects of process parameters on the uniformity of TiO_2 thin films deposited on Indium-Tin-Oxide (ITO) coated glass. Deposition experiments were carried out at temperatures ranging from 300℃ to 400℃ under the pressure of 0.5~2 torr in a cold-wall reactor which can handle 200mm substrate. It was found that the growth rate of TiO_2 was closely related to the reaction temperature and the ractant gas compositions. Apparent activation energy for the deposition rate was 62.7kJ/mol in the absence of O_2 and 100.4kJ/mol in the presence of O_2, respectively. Homogeneous reactions in the gas phase were promoted when the total pressure of the reactor was increased. Variance in the film thickness was less than a few percent, but at high deposition rates film thickness was less uniform. Effects of reaction temperature on TiO_2 thin film characteristic was investigated with SEM, XRD and AES.

1. INTRODUCTION

Thin film electroluminescent display (ELD) has been recognized as a promising technology for flat plate display. Being an emissive type device made of all solid state, it gives bright pictures and can function well in hostile environments. Thus it is used for air planes, plants as well as computer terminals to display information. Thin film ELD consists of thin film layers including light emitting layer and dielectric layers. It is known that dielectric layers play important roles for the good performance of ELD[1].

Various materials can be used as dielectric layers for ELD: silicon dioxide, silicon nitride, titanium oxide, tantalum oxide, aluminum oxide, ferroelectric material, etc. Thin films of TiO_2 have been proposed for a variety of dielectric application, because of its high dielectric constant[2] and excellent transmittance in the visible and near-IR-range[3]. As summarized in Table 1, extensive research has been made on the chemical vapor deposition (CVD) of titanium dioxide films[4~13] because in this way titanium dioxide can be fabricated as a dielectric for a thin film capacitor or as an antireflection coating on silicon. Several investigators employed $TiCl_4$[4] or titanium tetra-isopropoxide (TTIP)[6-8] or tetraethyl titanate[2] as titanium sources. Preparation of thin films by metal organic chemical vapor deposition (MOCVD) is gaining importance in various applications. In MOCVD vapors of metal organic compounds are introduced into a reactor and decomposed by heat, plasma, or laser beam. As the size of substrate increases in ULSI, flat panel display, solar cells, etc., the importance of thin film deposition technology for large areas also increases. For the production of large displays

Table 1. Summary of literature on CVD of titanium oxide thin film.

Ref. No.	Reactor type	Deposition conditions			E_a[d] (kJ/mol)	Characteristics
		Temp.[a] (℃)	Press.[b] (Pa)	Q[c] (sccm)		
7	APCVD[h]	227~700	n.a	1000	(w O_2) 27 (w/o O_2) 150	R_d[e](Å/min):17~1700 ρ[f](g/cm^3):2.40~2.49 R.I[g]:2.0~2.05
8	25mm quartz tube, hot wall	400~600	600	0~90 O_2 6~90 N_2	60	n.d
9	1×1cm fused quartz	200~400	n.a	2700 O_2 300 N_2	n.d	R_d(Å/min):15~20 R.I:2.0~2.4
10	58mm Bell-jar	300~600	400~1600	0~75% O_2 100~200 N_2	53	R_d(Å/min):50~600
11	cold wall	220~300	5.33~267	n.a	33at 20Pa 150at 267Pa	R_d(Å/min):50~5000
12	30mm quartz tube	300~500	667	80~140	n.d	n.d
13	hot wall LPCVD[i]	300~350	40~120	50~250 O_2 50~150 N_2	n.d	R_d(Å/min):1~15 ρ(g/cm^3):4.1 R.I:2.2~2.5
this study	cold wall LPCVD 200mm	300~400	67~267	50~200 O_2 50~200 N_2	(w O_2) 100.4 (w/o O_2) 62.7	R_d(Å/min):20~140

note) a : deposition temperature b : reactor pressure
c : gas flow rate d : activation energy
e : deposition rate f : film density
g : reflective index
h : atmospheric chemical vapor deposition i : low pressure chemical vapor deposition

or films of better quality low pressure process is preferred. Uniformity of film thickness depends strongly on the growth parameters, such as the substrate temperature and reactor pressure. For a given substrate temperature, non-uniformity in film thickness can be reduced simply by reducing reactor pressure.

In the present study, low pressure CVD for the deposition of titanium oxide was made aiming at the application for dielectric layers of large area thin film for ELD. Deposition experiments were carried out varying process parameters such as reaction temperature and pressure to investigate effects of them on deposition rate and uniformity of film thickness. Deposited TiO_2 thin films were characterized with XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy), and AES (Auger Electron Spectroscopy).

Ⅱ. EXPERIMENTAL

Fig. 1. shows the schematic diagram of the CVD reactor system used in this study. The reactor was a cold wall type made of stainless steel. Substrate of up to 200mm ID could be mounted on the heating block which was located in the center of the reactor. Temperature of the substrate was measured

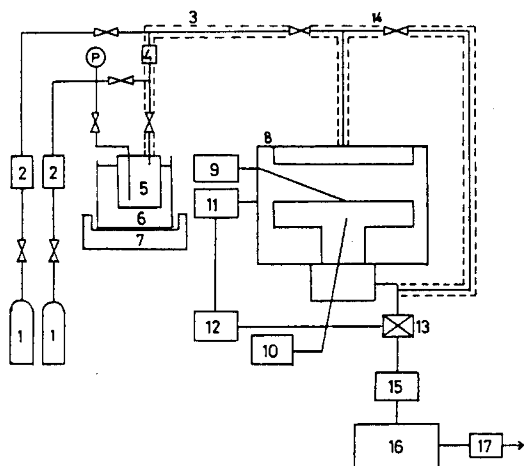

Fig. 1. Schematic diagram of CVD reactor system. 1, Gas cylinder; 2, Mass Flow Controller; 3, Heated line; 4, Needle valve; 5, Bubbler; 6, Water bath; 7, Magentic stirrer; 8, Reactor; 9, Thermocouple; 10, Heating block; 11, Capacitance manometer; 12, Pressure controller; 13, Throttle valve; 14, By-pass line; 15, Alumina trap; 16, Mechanical pump; 17, Oil filtration.

with a K-type thermocouple in contact with it. Reactant gases were introduced into the reactor through showerhead. The distance from the showerhead to the substrate could be varied between 5cm and 10cm by linear movement of the heating block. TTIP of high purity(99.999%) was put into a bubbler which was maintained within ±1℃ in a thermostat. Nitrogen was used as carrier gas for TTIP. Oxygen was also supplied to the reactor to obtain films of good quality and to eliminate carbon incorporation in the films. Mass flow controllers were used for the control of gas flow rates. Gas line from the bubbler to the reactor inlet was kept at 30∼40℃ above bubbler temperature to avoid condensation of TTIP in it. Pressure of the reactor was controlled with a feedback loop consisting of a capacitance pressure gauge and a throttling valve downstream of the reactor. Gases from the reactor was evacuated by a mechanical pump.

ITO-coated glass was used as substrate. It was cutted into 1.5×1.5cm pieces and rinsed in acetone. For each run of deposition experiment four pieces of ITO glass were mounted onto the heating block at radial positions 0, 3, 6, 9cm from the center, respectively.

Deposition experiments were carried out varying reactor pressure, substrate temperature, flow rate of nitrogen carrier gas and oxygen, bubbler temperature, and the distance between the showerhead and the substrate.

Growth rate of TiO_2 was determined by weighing each sample before and after the deposition experiment, and dividing the weight change by deposition time. Growth rates are presented here in units of Å/min, based on the real density of TiO_2 (1Å/min$=1.99\times10^{-11}$ mol/cm^2/s). Although the densities of thin films show some variation depending on O_2 flow rate and temperature, we observed these values were nearly constant within range of 2.4∼2.5g/cm^3 from the thickness of thin films obtained by SEM. Therefore, in this study the thickness of films determined by weight gain can be valid within a few percent error range.

Ⅲ. RESULTS AND DISCUSSION

Effects of process parameters

Effects of deposition temperature

Fig. 2. shows effects of deposition temperature on the deposition rates and uniformity which are mean values and standard deviation of deposition rates on the four substrates mounted onto different radial position from the center. Deposition rates and variance of them increased with temperature in the absence of O_2, but above 330℃ they decreased with further increase of temperature. Below 330℃ uniformity of deposition rate was in the range from 1 to 5%. In the presence of O_2 deposition rate exhibited maximum value at 350℃. The decrease of the TiO_2 deposition rate at temperatures above 350℃ is believed due to decreased TTIP concentration at the substrate surface caused

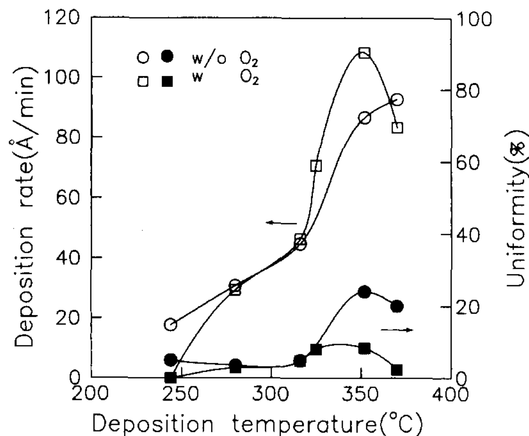

Fig. 2. Effects of deposition temperature on TiO_2 deposition rate. Pressure 1 torr, N_2 flow rate 100 sccm. ○, □, deposition rate; ●, ■, uniformity.

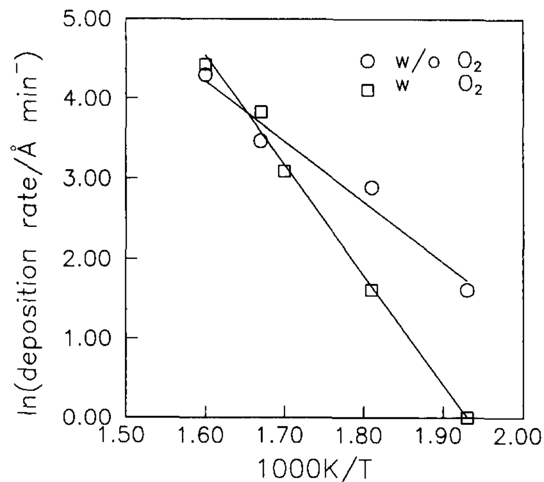

Fig. 3. Arrhenius plot for deposition rate of TiO_2 film. Deposition conditions are the same as in Fig. 2.

by homogeneous reactions of reactant species in the gas phase[10]. It is generally accepted that deposition rate decreases with temperature in the homogeneous reaction regime[14]. The appearance of the maximum deposition rate indicates the onset of homogeneous reactions. On the other hand, in the view of MOCVD reaction mechanisms it is also known that in the regime, where deposition rates increase with substrate temperature, pyrolysis or oxidation rates of reactants on the substrate surface is rate-determining, while in the high temperature deposition regime, where deposition rates depend upon gas flow rates, mass transfer of reactants to the substrate surface is rate-determining[15].

Arrhenius plots of observed deposition rates are shown in Fig. 3. In general deposition is controlled by mass transfer when activation energy is less than 41.8kJ/mol, and controlled by surface reaction when activation energy is much greater than 41.8kJ/mol. Apparent activation energy obtained from Fig. 3 by least mean squares method was 62.7kJ/mol in the absence of O_2, and 100.4kJ/mol in the presence of O_2. Therefore, the deposition reaction of TiO_2 is controlled by surface reaction under the experimental conditions.

Effects of reactor pressure

Fig. 4. shows effects of reactor pressure on the deposition rates of TiO_2 at 320℃ and 360℃.

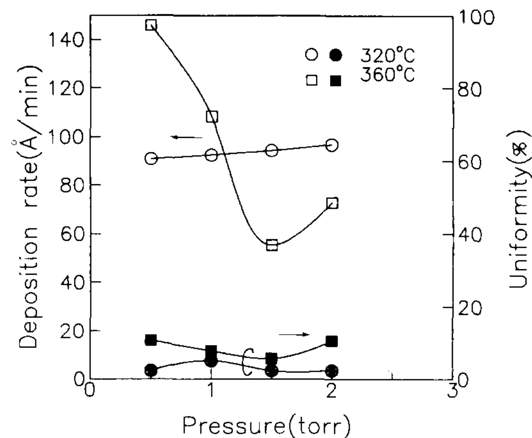

Fig. 4. Effects of reactor pressure of TiO_2 deposition rate. N_2 flow rate 100 sccm, O_2 flow rate 100 sccm. ○, □, deposition rate; ●, ■, uniformity.

Change in deposition rate with pressure was insignificant at deposition temperature of 320 ℃. However, deposition rate decreased with pressure at 360℃. This could be explained by the fact that molecular diffusivity of reactants decreases as well as the residence time of reactants increases according to pressure increase. Homogeneous gas-phase reaction, which are generally favorable under conditions

of long gas residence time and high reaction pressure, should lead to a decrease in the amount of reactive species participating in the heterogeneous reaction for thin film deposition on substrate. Therefore, it can be also construed that homogeneous reactions are significant as discussed in Fig. 2 under these conditions.

Effects of oxygen flow rate

Fig. 5. shows effects of oxygen flow rate on the deposition rates of TiO_2 to be insignificant. The deposition rate of TiO_2 film is independent of the oxygen flow rate and nearly equal to that deposited in an inert gas, and it indicates that the main reaction in TiO_2 deposition is pyrolysis of TTIP. This results are consistent with these of Tominaga et al[7]. But Takahashi et al[8]. Reported that the change of deposition characteristics was not observed for the oxygen flow rate.

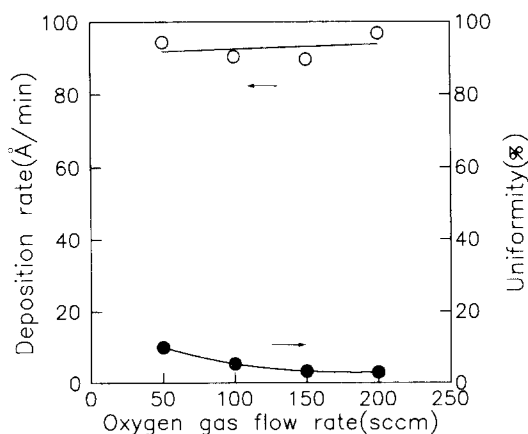

Fig. 5. Effects of oxygen flow rate on TiO_2 deposition rate. Temperature 340℃, Pressure 2 torr, N_2 flow rate 100 sccm. ○, deposition rate; ●, uniformity.

Effects of carrier gas flow rate

Fig. 6. shows that deposition rate increases with the increase of carrier gas flow rate. This proves that under test condition, the deposition rate of TiO_2 film can be controlled within the range of 60~120Å/min by adjusting the carrier gas flow rate and the source temperature.

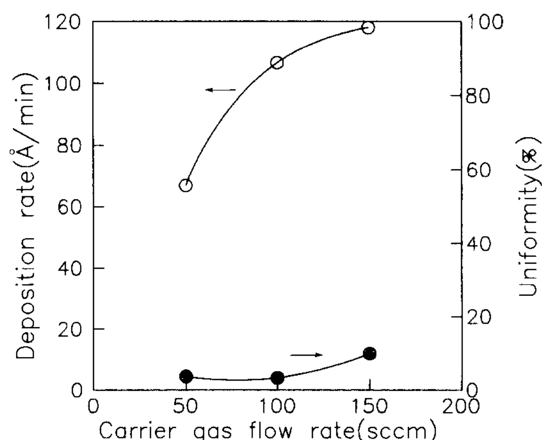

Fig. 6. Effects of carrier gas flow rate on TiO_2 deposition rate. Temperature 340℃, Pressure 2 torr, O_2 flow rate 200 sccm. ○, deposition rate; ●, uniformity.

Effects of bubbler temperature

Deposition rate increased with bubbler temperature. Logarithmic plots of observed deposition rate against reciprocal temperature showed a good linear relationship, the slope of which is approximately proportional to the heat of vaporization of TTIP. The estimated value of heat of vaporization from Fig. 7. is 58.2kJ/mol which is very close to the reported value of 61.5kJ/mol[16]. This also suggests that

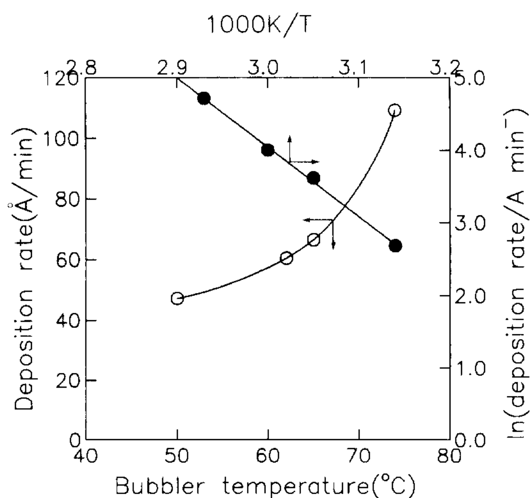

Fig. 7. Effects of bubbler temperature on TiO_2 deposition rate. Temperature 340℃, Pressure 2 torr, N_2 flow rate 100sccm, O_2 flow rate 200sccm.

deposition rate is linearly proportional to the vapor concentration of TTIP.

Effects of distance between showerhead and substrate

Fig. 8. shows effects of distance between

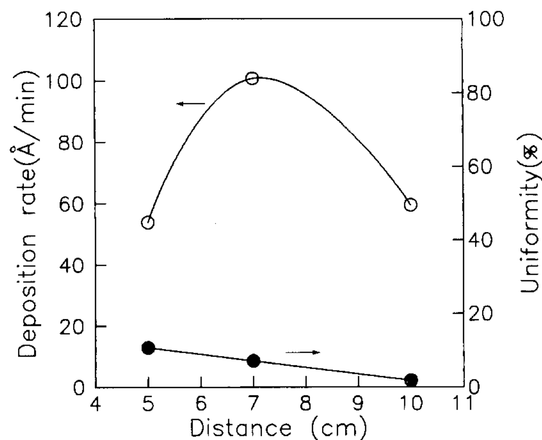

Fig. 8. Effects of distance between the showerhead and the substrate on TiO_2 deposition rate. Temperature 360℃, Pressure 2 torr, N_2 flow rate 100 sccm, O_2 flow rate 200sccm. O,deposition rate; ●, uniformity.

showerhead and substrate on the deposition rates of TiO_2. It was observed that maximum deposition rate appeared while uniformity was decreased with distance between showerhead and substrate. Although it is difficult to draw any conclusion from the figure it implies importance of reaction path involving precursors of CVD in the gas phase and physical transport of reactants to deposition surface. More studies such as analysis of reactants in the reactor and spatial distribution of their composition are needed for better understanding.

Properties of TiO_2 film

Fig. 9. shows XRD patterns of TiO_2 films deposited at 300℃ and 350℃. XRD peak intensity increased with deposition temperature. It indicates the size of crystal increases with deposition temperature.

Fig. 10. shows surface morphology of TiO_2 films deposited at different temperatures. Surface morphology of TiO_2 films deposited at

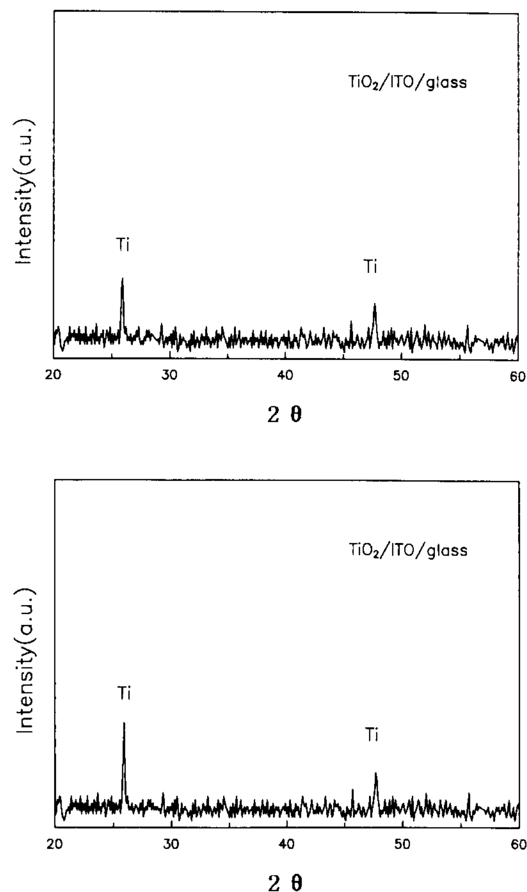

Fig. 9. XRD patterns of TiO_2 films. Deposition temperatures (a) 300℃, (b) 350℃.

(a) 300℃ and (b) 350℃ support XRD peaks of Fig. 9. On the contrary, TiO_2 film deposited at (c) 370℃ shows that the film is in a microcrystalline state. It implies that the size of the TiO_2 crystal decreases with increase of temperature in this particular regime of deposition as the size of the nucleus and the growth rate of TiO_2 decrease with increasing temperature[17]. At temperatures above 350℃ microcrystallines were formed due to shift of deposition mechanism with deposition temperature.

In order to study the composition of the TiO_2, AES of the film was carried out with Perkin-Elmer PHI 670 Scanning Auger Microprobe (SAM) operated at primary electron energy at 5 KeV. In this case, the thickness of the film was about 2000 Å. Peaks of elements

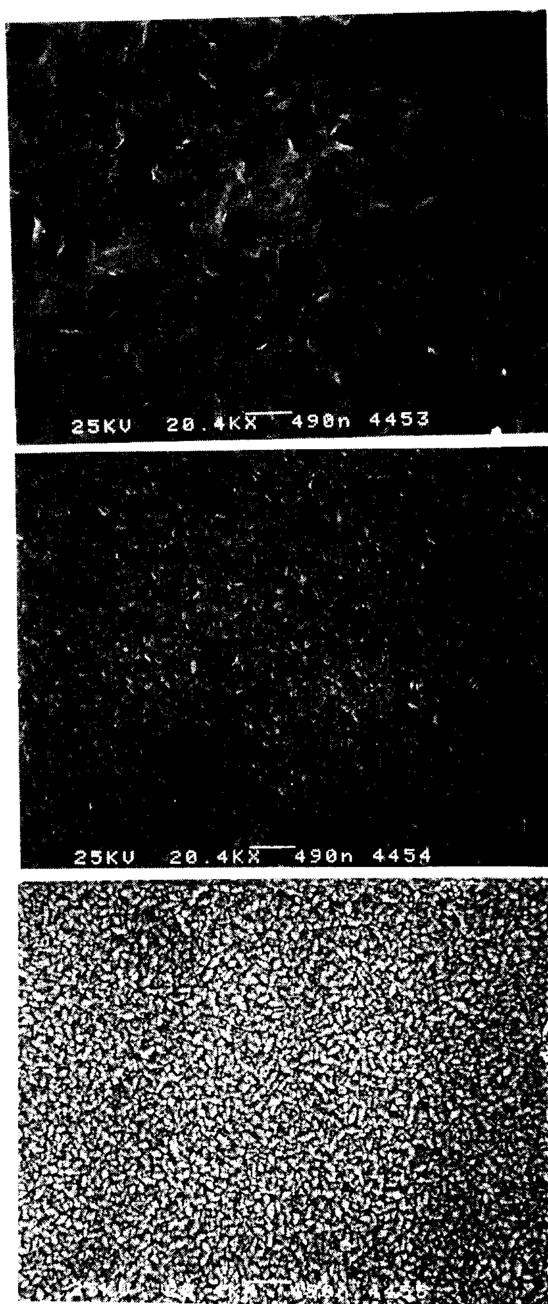

Fig. 10. Surface morphology of TiO_2 films. Deposition temperatures (a) 300℃, (b) 350℃, (c) 370℃.

representing TiO_2 film were seen in the spectra of Fig. 11. In order to identify impurities in the TiO_2 film, Auger depth profiles were obtained at room temperature. Fig. 12 shows carbon exists in the TiO_2 deposition layer. This suggests that carbon in the TiO_2 film is not surface contamination caused by handling of the film but from the decomposition of reactant, $Ti(OC_3H_7)_4$.

Ⅳ. CONCLUSION

With TTIP as the precursor for CVD titanium oxide could be deposited with good uniformity on ITO-coated glass. At deposition temperatures below 330℃ deposition rate of TiO_2 increased with deposition temperature indicating reaction controlled deposition regime. But at higher temperature deposition rate decreased with further increase of temperature implying quite a different deposition regime. Effects of pressure on the deposition rate also showed dominant role of temperature. At 320℃ deposition rate was not sensitive to pressure while deposition rate decreased sharply with pressure at 360℃.

Effects of gas flow rate and the distance between showerhead and substrate on deposition rate also indicate complicated interactions between chemical reactions and physical transport of reactant species to deposition surface. More studies will be needed to elucidate them.

References

1. L. E. Tannas, Jr., "Flat panel Displays and CRTs", Van Nostrand Reinhold Co., New York, Chapt. 8, (1985)
2. T. Nakayama, K. Onisawa, M. Fuyama, and M. Hanazono, "TiO_2/SiO_2 Multilayer Insulating Films for ELDs", J. Electrochem. Soc., **139,** 1204 (1992)
3. H. K. Pulker, "Characterization of Optical Thin Films", Appl. Opt., **18,** 1969 (1979)
4. R. N. Ghoshtagore, and A. J. Noreika, "Growth Characteristics of Rutile Film by CVD", J. Electrochem. Soc., **117,** 1310 (1970)
5. Y. Takahashi, K. Tsuda, K. Sugiyama, H. Minoura, D. Makino, and M. Tsuiki, "Chemical Vapour Deposition of TiO_2 Film using an Organometalic Process and its Photoelectrochemical Behaviors", J. Chem.

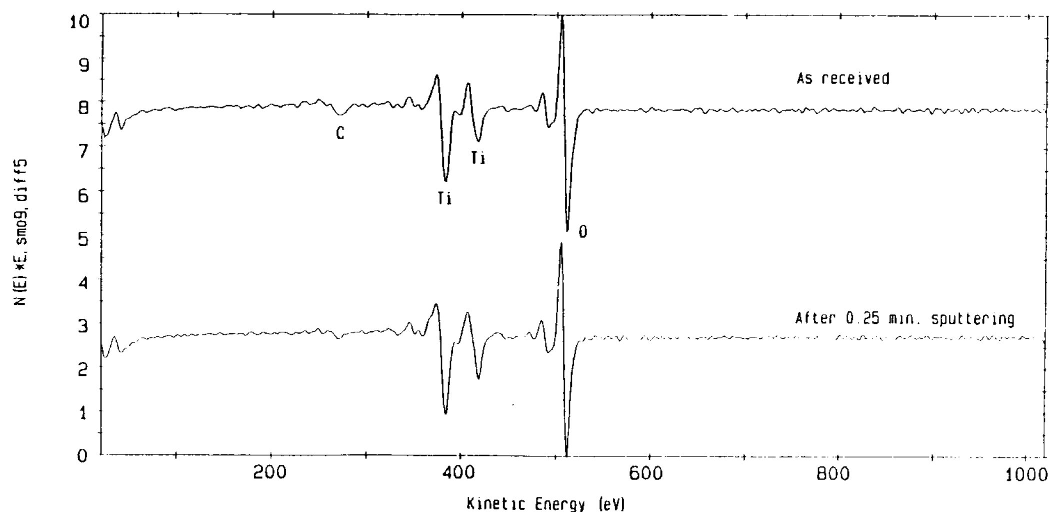

Fig. 11. Auger spectrum of the surface of TiO_2 film. Deposition temperature 300℃, Pressure 2 torr, N_2 flow rate 100 sccm, O_2 flow rate 200 sccm.

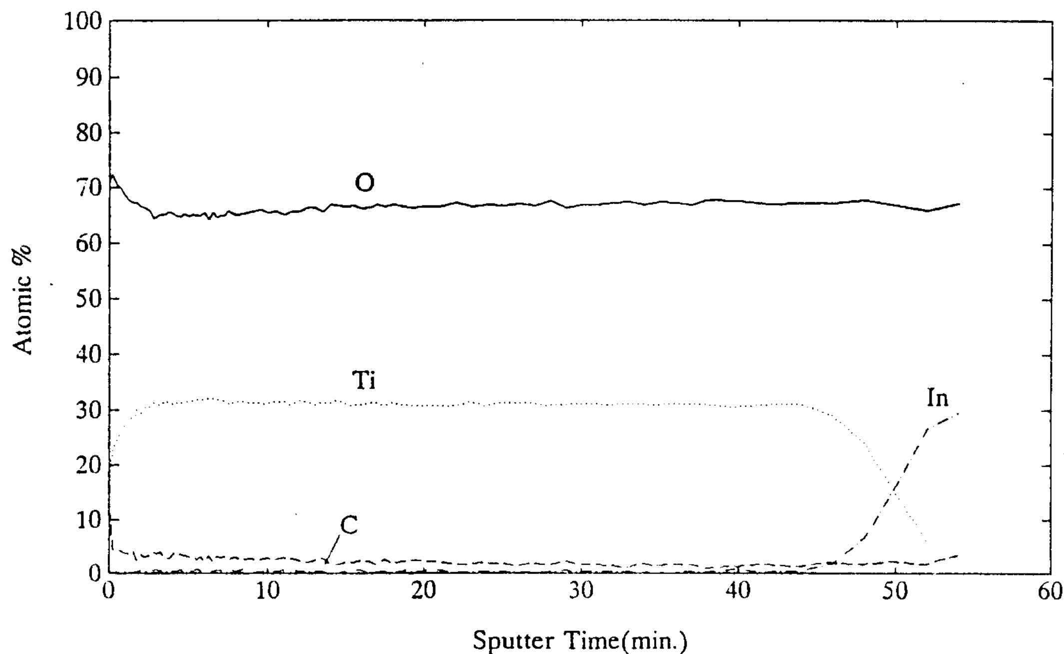

Fig. 12. Auger depth profile of TiO_2 film. Deposition conditions are the same as in Fig. 11.

Soc. Faraday Trans. Inst., **77,** 1051 (1981)

6. H. J. Hovel, "TiO_2 Antireflection coatings by a low temperature spray process", J. Electrochem. Soc., **125,** 983 (1978)
7. K. Tominaga, M. Miyajima, Y. Sakashita, H. Segawa, and M. Okada, "Preparation of C-Axis-Oriented PLT Thin Films by the Metalorganic Chemical Vapor Deposition", Japan. J. Appl. Phys., **29,** L1874(1990)

8. Y. Takahashi, H. Suzuki and M. Nasu, "Rutile Growth and TiO_2 Films deposited by vapour-phase decomposition of Isopropyl Titanate", J. Chem. Soc. Faraday Trans. Inst., **81**, 3117 (1985)
9. T. Fuyuki, and H. Matsunami, "Electronic Properties of the Interface between Si and TiO_2 Deposited at very low Temperatures", Japan. J. Appl. Phys., **25**, 1288 (1986)
10. M. Okada, K. Tominaga, T. Araki, S. Katayama, and Y. Sakashita, "Metalorganic Chemical Vapor Deposition of c-Axis Oriented PZT Thin Films", Japan. J. Appl. Phys., **29**, 718 (1990)
11. K. L. Siegering, and G. L. Griffin, "Kinetics of Low Pressure Chemical Vapor Deposition of TiO_2 from Titanium Tetraisopropoxide", J. Electrochem. Soc., **137**(3), 814 (1990)
12. T. K. Won, S. G. Yoon, and H. G. Kim, "Compositional Analysis and Capacitance-Voltage Properties of TiO_2 Films by Low Pressure Metal-Organic Chemical Vapor Deposition", J. Electrochem. Soc., **139**, 3284 (1993)
13. N. Rausch, and E. P. Burte, "Thin TiO_2 Films Prepared by Low Pressure Chemical Vapor Deposition", J. Electrochem. Soc., **140**, 145 (1993)
14. K. J. Sladek, "The Role of Homogeneous Reaction in Chemical Vapor Deposition", J. Electrochem, Soc., **118**, 654 (1971)
15. J. Saraie, J. Kwon, and Y. Yodogawa, "Chemical Vapor Deposition of Al_2O_3 Thin Films under Reduced Pressure", J. Electrochem. Soc., **132**, 890 (1985)
16. Soon-Gil Yoon, and Ho-Gi Kim, "Preparation and Deposition mechanism of Ferroelectric $PbTiO_3$ Thin Films by Chemical Vapor Deposition", J. Electrochem. Soc., **135**, 3137 (1988)
17. P. Lee, D. Mckenna, D. Kapur, and K. F. Jensen, "MOCVD in Inversed Stagnation Point Flow", J. Cryst. Growth, **77**, 120 (1986)