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Modeling the current density in sol–gel electrophoretic deposition of titania thin film

S. Ghannadi[a], H. Abdizadeh[a,b], M.R. Golobostanfard[a,*]

[a]School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P.O. Box 14395-553, Tehran, Iran
[b]Center of Excellence for High Performance Materials, University of Tehran, P.O. Box 14395-553, Tehran, Iran

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Abstract

This work deals with the combination of sol–gel process and electrophoretic deposition. Modeling of current density during electrophoretic deposition is a simple analysis done to understand the rate of deposition, which allows predicting thickness of deposited film as a function of sol–gel parameters. In this study, titania sol as a colloidal suspension is used to investigate parameters affecting the deposition rate. The sols were synthesized by controlled hydrolysis and condensation of titanium alkoxide. It is shown that the rate of deposition enhances with increasing precursor concentration and rate of hydrolysis. Therefore, increasing the precursor concentration and the water content causes higher hydrolysis and hence higher film thickness. However, increasing the acid catalyst content leads to lower film thickness. Effect of water content on increasing the film thickness is more noticeable than those of precursor concentration and acid catalyst content.

Keywords: A. Sol–gel processes; D. TiO_2; Electrophoretic deposition; Current density modeling

1. Introduction

Titanium dioxide is a well-known material due to its specific properties and extensive applications such as photocatalysts [1], gas sensors [2], and solar cells [3]. Many different methods such as physical vapor deposition [4], chemical vapor deposition [5], spin coating [6], dip coating [7] and electrophoretic deposition [8] have been used for synthesizing nanostructured titania coatings. Electrophoretic deposition (EPD) is an interesting method for preparing oxide coatings owing to its high deposition rate. EPD is based on the movement of charged particles in a stable suspension towards the opposite electrode by applying an electric field. Both aqueous [9–11] and non-aqueous [12–14] suspensions have been used for EPD of TiO_2, whereas organic solvents such as acetone and alcohols are usually preferred over water due to the occurrence of hydrolysis reaction at very low voltages in case of aqueous suspension [15].

The sol–gel method has so many advantages for synthesis of TiO_2 coatings. However, low film thickness is the major restriction of using some conventional deposition method such as spin and dip coating methods. One way to synthesize thicker films is combining the sol–gel method and EPD process. Colloidal sol is an ideal medium for electrophoretic deposition due to some advantages such as high homogeneity and good stability. Therefore, sol–gel electrophoretic deposition can be simply controlled by adjusting the sol parameters.

EPD can be described as an electrical circuit with electrical parameters such as voltage, current, and resistance. With this attitude, several models have been developed to predict the kinetics of EPD. Van der Biest et al. used this technique to derive yield of deposition as a function of time [16].

Although EPDs based on sol have been reported to prepare thick oxide coatings [17–20], the correlation between alkoxide sol–gel parameters and the deposition rate of EPD was never investigated. In alkoxide sol–gel, the gelation time can be strongly affected by the hydrolysis rate. The aim of present work is to model the kinetics of alkoxide sol–gel electrophoretic deposition of titania and investigate possible correlation between the rate of deposition and that of hydrolysis in acid catalyst controlled alkoxide titania sol. For this purpose,

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*Corresponding author. Tel.: +98 91 22300382; fax: +98 21 88006076.
E-mail addresses: Bostanfr@ut.ac.ir, Mohammadreza.Golbostanfard@gmail.com (M.R. Golobostanfard).

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the effects of precursor concentration, water content, and acid catalyst content on film thicknesses were considered.

2. Materials and methods

The procedure of preparing titania sols was similar to those reported elsewhere [6]. Typically, titanium tetra isopropoxide (TTIP, 98%, Merck) was used as a precursor and dissolved in ethanol (EtOH, 99.9%, Merck) under stirring for 15 min. The solution containing deionized water (DIW, 18.2 MΩ), nitric acid (HNO_3, 65%, Merck), and ethanol (EtOH, reagent grade, Merck) was prepared and added drop-wise to the TTIP solution under vigorous stirring. The final sol composition was $TTIP:H_2O:HNO_3 = 1:4:0.5$ in molar ratio with 0.17 M TTIP concentration. Sols with different TTIP concentrations of 0.225 and 0.34 M were also considered. Moreover, in order to investigate the effect of water content on deposition rate, sols with $[H_2O]/[TTIP] = 1$, 2, and 8 were prepared. Furthermore, sol with $[HNO_3]/[TTIP] = 0.25$ was prepared to study the effect of acid catalyst content on deposition rate. In all samples while one parameter was changed, the other parameters were held constant. The sample composition and gel time of each sol are brought together in Table 1.

Electrophoretic deposition (EPD) was performed on FTO (15 Ω/□, Dyesol) substrate as cathode and a plate of stainless steel as anode. Two electrodes were 1 cm apart. A constant voltage of 5 V was applied between two electrodes during the deposition. The same trend for film deposition was observed in other voltages. However, the deposition voltage of 5 V is an optimum value for investigating the effect of sol parameters on deposition rate. The deposition time was set at 1 min. After 1 min deposition, variation in the current density with time is negligible. After deposition, the coated substrates were dried at 100 °C for 10 min and subsequently calcined at 450 °C for 1 h. The current density during the deposition was recorded by a computer connected multimeter (GDM 396, GW Insteck). Also, field emission scanning electron microscopy (FESEM, Hitachi S4160) was used to compare the surface morphology and thickness of the deposited films.

Table 1
Concentration, composition (molar ratio) and gel time of the samples.

Sol	TTIP concentration (M)	$[H_2O]/[TTIP]$	$[HNO_3]/[TTIP]$	Gel time (days)
M	0.170	4	0.50	5
C2	0.255	4	0.50	5
C3	0.340	4	0.50	4
H1	0.170	1	0.50	10
H2	0.170	2	0.50	7
H8	0.170	8	0.50	2
A2	0.170	4	0.25	3

3. Calculation

Titania sol includes nanoclusters that are formed during hydrolysis and condensation. These nanoclusters have positive surface charge ($\zeta > 0$) and form a deposit on the cathode (Fig. 1a). The equivalent circuit of electrophoretic deposition is the same as reported elsewhere (Fig. 1b) [16]. The current path is divided into two sections in the model: one section is related to the sol, and the other to the deposit conduction. In each section, two parallel resistances are considered: R_{sol} and $R_{cluster}$ which correspond to the resistance of counter-ions and titania nanoclusters, respectively.

According to Fig. 1, if a constant voltage (V) was applied between two electrodes, the total electric current passing through the deposition cell can be calculated from Ohm's law. Hence, by deriving from Ohm's equation with respect to time, we have

$$R\frac{dI}{dt} + I\frac{dR}{dt} = 0 \tag{1}$$

The total resistances are equal to sum of R_1 and R_2, where R_1 is the resistance of the sol and R_2 is the resistance of the deposited layer. Since the distance between two electrodes (d) is much larger than the thickness of deposit (δ) and in order to facilitate the calculation, R_2 variation in time is assumed to be zero. Then, substitution of V/I in R_1 gives

$$\frac{-dI}{I^2} = \frac{1}{V}\frac{dR_1}{dt}dt \tag{2}$$

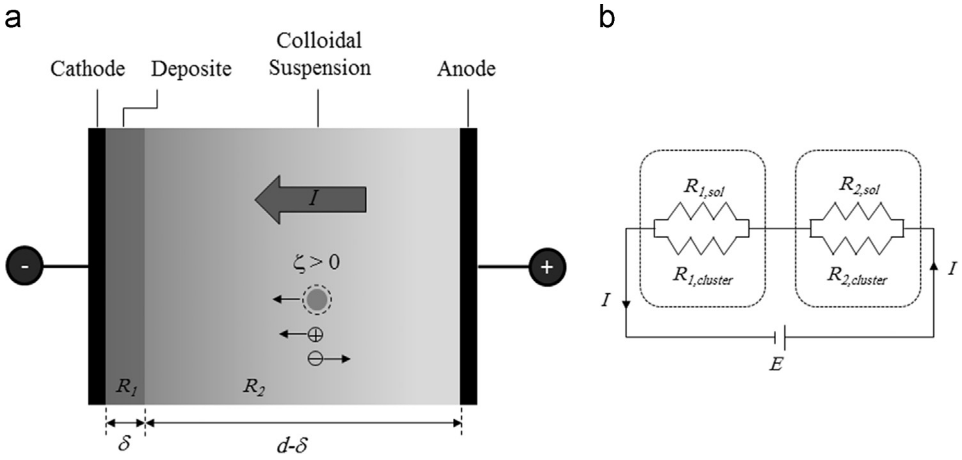

Fig. 1. (a) Schematic of the EPD cell and (b) equivalent circuit of EPD.

The resistance in Section 1 can be obtained by the following equation [16]:

$$R_1 = \frac{\rho_{sol}\rho_{cluster}}{A(\rho_{sol} + \rho_{cluster})}\delta \tag{3}$$

where ρ_{sol} is the ionic resistivity of titania sol, $\rho_{cluster}$ is the resistivity of deposited titania nanoclusters, and A is the deposit surface area. Since the thickness of deposit is changed with deposition time, deriving Eq. (3) leads to

$$\frac{dR_1}{dt} = B\frac{d\delta}{dt} \tag{4}$$

where

$$B = \frac{\rho_{sol}\rho_{cluster}}{A(\rho_{sol} + \rho_{cluster})} \tag{5}$$

Amount of deposited mass is given by

$$w = \rho_{deposit}V_{deposit} = \rho_{deposit}A\delta \tag{6}$$

then, the time derivative of Eq. (6) reads

$$\frac{d\delta}{dt} = \frac{1}{\rho_{deposit}A}\frac{dw}{dt} \tag{7}$$

Furthermore, the deposition rate, proposed by Hamaker [21], expresses the following equation:

$$\frac{dw}{dt} = f\mu EAC \tag{8}$$

where C is the concentration of electrophoretic media, E is the applied voltage, and f is a dimensionless factor which takes into account that not every particle moves toward the electrode

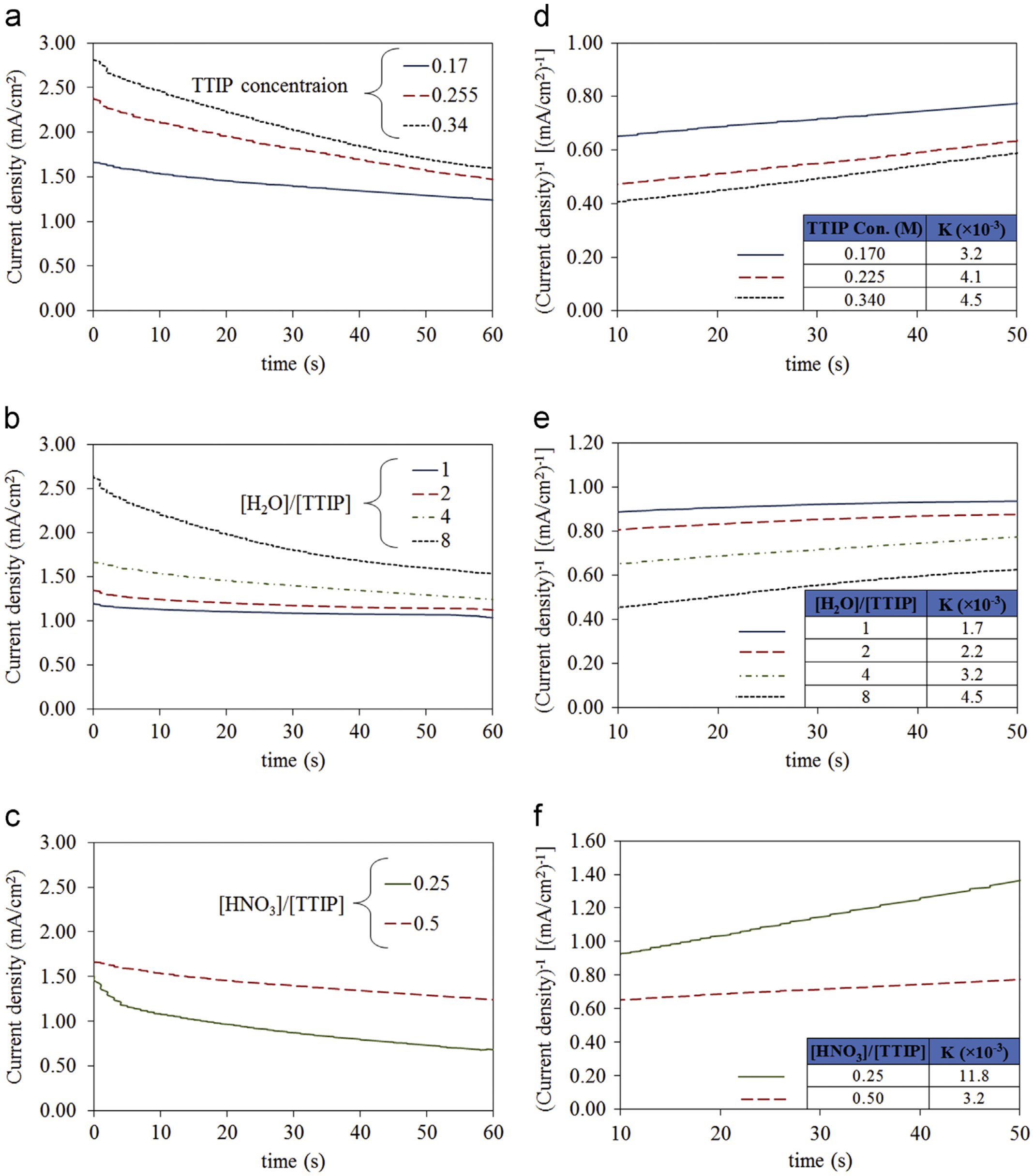

Fig. 2. Plots of current density versus deposition time at different (a) TTIP concentration (M, C2 and C3), (b) $[H_2O]/[TTIP]$ (M, H1, H2 and H8), and (c) $[HNO_3]/[TTIP]$ (M and A2) ratios. Plots of inverse current density versus deposition time at different (d) TTIP concentration, (e) $[H_2O]/[TTIP]$, and (f) $[HNO_3]/[TTIP]$ ratios. Insets show calculated K values.

will be eventually deposited ($f \leq 1$). μ is the electrophoretic mobility that is related to the surface charge of nanoclusters, dielectric constant of medium, and viscosity of the sol. With regard to Eqs. (4), (7) and (8) the following equation is resulted:

$$\frac{dR}{dt} = \frac{f\mu ECB}{\rho_{deposit}} \tag{9}$$

Hence, according to Eq. (1)

$$\frac{-dI}{I^2} = \frac{f\mu CB}{\rho_{deposit}} dt \tag{10}$$

Integrating the above equation gives

$$\frac{1}{I} = Kt + \frac{1}{I_s} \tag{11}$$

where I_s is the current process in the initial time and

$$K = \frac{f\mu CB}{\rho_{deposit}} \tag{12}$$

Therefore, the term K can be calculated by plotting inverse current density versus time. Eq. (12) shows that K is related to mobility of electrophoretic (μ) and concentration (C) which are two significant parameters in the kinetics of deposition.

4. Results and discussion

Fig. 2 illustrates the plots of current density and inverse current density versus deposition time for different TTIP concentrations, $[H_2O]/[TTIP]$, and $[HNO_3]/[TTIP]$ ratios. The plots of current density (Fig. 2(a)–(c)) reveals that the current density of EPD process decreases with time due to the

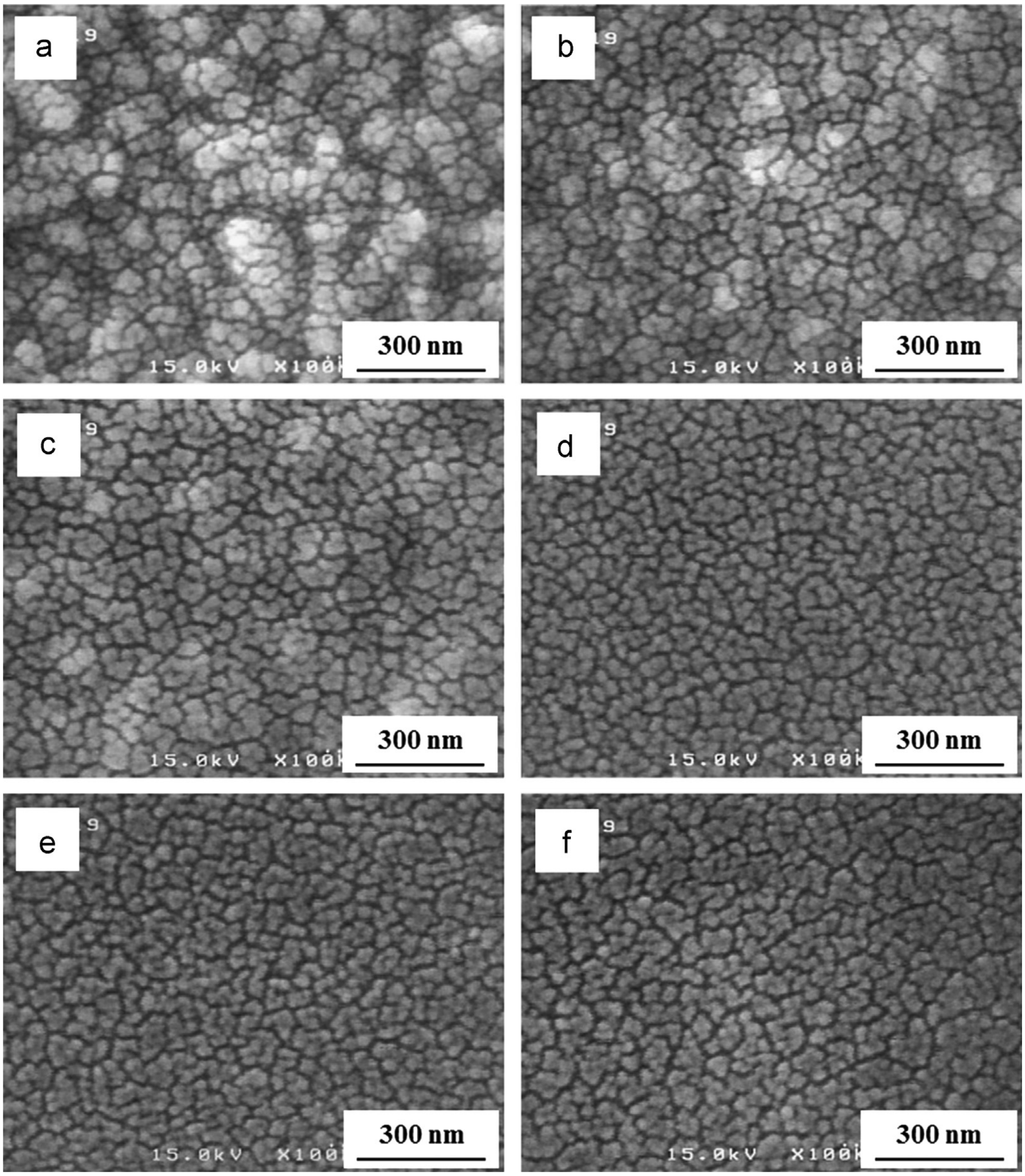

Fig. 3. FESEM images of TiO_2 thin films: (a) H1, (b) H2, (c) M (d) H8, (e) C3, and (f) A2 samples.

formation of insulation layer and increasing of the film thickness during EPD process.

Fig. 2d presents the plots of inverse current density versus time for different TTIP concentrations. It can be seen that the slope of inverse current density versus time (K) increases with increasing the TTIP concentration. From Eq. (8), it could be inferred that the rate of deposition increases with increasing the amount of TiO_2 nanoclusters. Thus, increasing the TTIP concentration leads to increase in number of TiO_2 nanoclusters in the sol.

In sol–gel electrophoretic, the amount of TiO_2 nanoclusters are determined by the rate of hydrolysis and condensation reaction of TiO_2 sol. The hydrolysis reaction can be written as follows in alkoxide sol–gel processing:

$$M(\mathrm{OR})_n + x\mathrm{H_2O} \rightarrow M(\mathrm{OH})_x(\mathrm{OR})_{n-x} + x\mathrm{ROH} \tag{13}$$

The rate of hydrolysis controls the reaction; that is, [OH]/[OR] ratio determines the mono-sized particles in the sol. The condensation of the hydrolyzed species occurs in the next step:

$$2[M(\mathrm{OH})_x(\mathrm{OR})_{n-x}] \rightarrow \mathrm{M(OR)}_{n-x}(\mathrm{OH})_{x-1}-\mathrm{O}-\mathrm{M(OR)}_{n-x-1}(\mathrm{OH})_x + \mathrm{ROH} \tag{14}$$

As can be seen in Fig. 2e, increasing the water content increases K value. According to hydrolysis reaction (13), the higher the amount of water to alkoxide ratio, the higher the rate of hydrolysis and the higher the [OH]/[OR] ratio. Since the nucleophilic character of [OH] group is more than [OR] group, the surface charge of clusters becomes more positive by increasing the [OH]/[OR] ratio. Therefore, the electrophoretic mobility (μ) increases and leads to increase in the rate of deposition.

Another way to control the rate of hydrolysis is using the catalyst to adjust the pH of the sol. Hydrolysis rate can be controlled by protonating of [OR] groups in the presence of $[H_3O]^+$ [22]. Therefore, it is expected that the rate of hydrolysis reduces with increasing the amount of acid catalyst. Thus, the higher amount of acid catalyst enhances the net surface charge, and hence increases the current density (Fig. 2c). However, the rate of deposition has an inverse relationship with the amount of acid catalyst according to Fig. 2f due to decrease in the hydrolysis reaction.

The surface morphologies of TiO_2 thin films synthesized by sol–gel electrophoretic deposition are presented in Fig. 3. All the films are dense and compact with an average grain size of about 30 nm. Fig. 3(a)–(d) shows that the uniformity of microstructure in the film surface increases with increasing of water to alkoxide ratio. This can be due to the fact that the rate of deposition is high at higher water to alkoxide ratios and nanoclusters completely cover the surface of FTO substrate. Also, it could be seen that increasing TTIP concentration or decreasing acid catalyst content leads to uniform distribution of titania nanoparticles on surface of the films (Fig. 3e and f).

Fig. 4 illustrates the thickness of deposited films by sol–gel electrophoretic deposition. The film thickness increases from 360 to 630 nm with increasing the water to alkoxide ratio from 4 to 8. Also, the film thickness increases from 360 to 420 nm by decreasing the acid catalyst to alkoxide ratio. Furthermore,

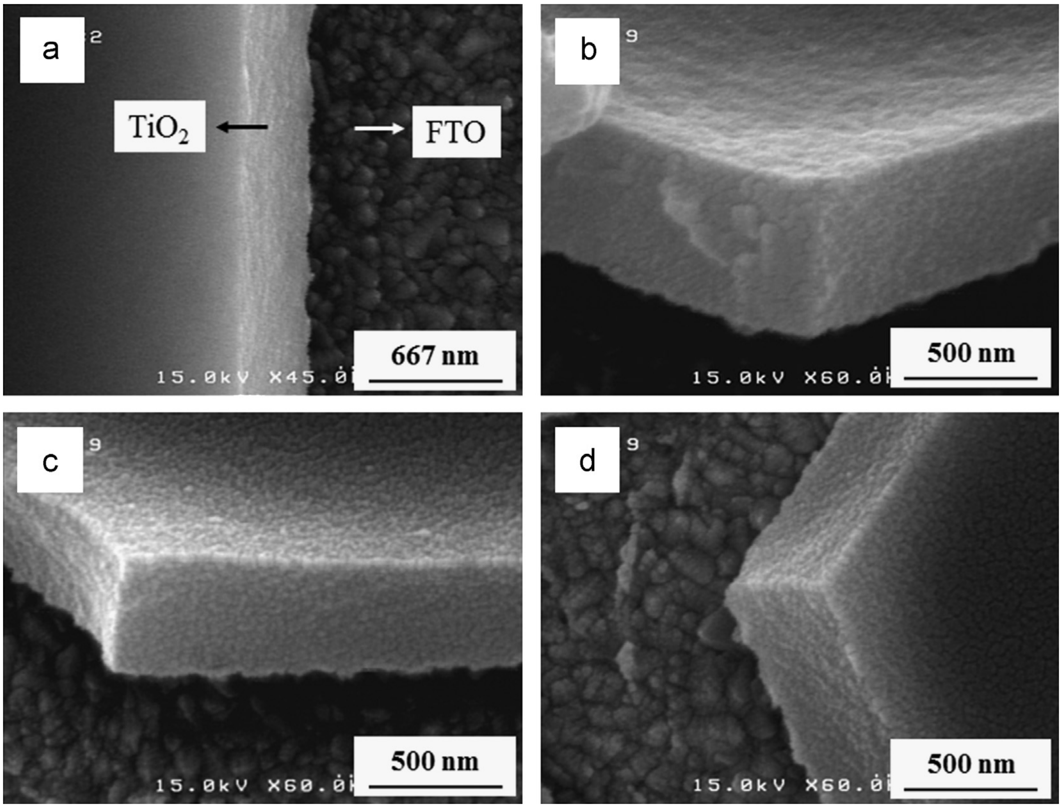

Fig. 4. Thickness of deposited TiO_2 thin films for (a) M, (b) H8, (c) C3, and (d) A2 samples (FTO substrate is distinguished from deposited TiO_2 layer in (a)).

by doubling TTIP concentration, the film thickness increases from 360 to 480 nm. It is obvious that gelation time becomes faster with increasing the rate of hydrolysis. The gelation time of H8 is less than that of other sols as presented in Table 1. Thus, it is clear that the effect of water to alkoxide ratio on the rate of deposition is more noticeable than acid catalyst content and TTIP concentration with regards to higher hydrolysis rate. These thickness variations are in good agreement with the modeling and the plots of inverse current density versus time during deposition.

5. Conclusions

In this article, we have proposed the model of current density versus time for sol–gel electrophoretic deposition. The model represents direct relation between the slope of inverse current density plots (K) and the rate of deposition. The rate of hydrolysis reaction in titania sol influences the current density and the rate of deposition. Parameters such as TTIP concentration, water content, and acid catalyst content play different roles in the rate of deposition under a fixed voltage. The rate of hydrolysis and subsequently the film thickness increases by increasing the water content and the TTIP concentration. However, increasing the amount of acid catalyst decreases the rate of deposition. It was found that doubling the amount of water content is more effective than taking the amount of acid catalyst content to half or doubling the TTIP concentration.

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References

[1] N. Negishi, T. Iyoda, K. Hashimoto, A. Fujishima, Preparation of transparent TiO_2 thin film photocatalyst and its photocatalytic activity, Chemical Letters 24 (1995) 841–842.

[2] K. Galatsis, Y.X. Li, W. Wlodarski, E. Comini, G. Faglia, G. Sberveglieri, Semiconductor MoO_3–TiO_2 thin film gas sensors, Sensors and Actuators B 77 (2001) 472–473.

[3] B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature 353 (1991) 737–740.

[4] K. Rao, S. Mohan, Optical properties of electron-beam evaporated TiO_2 films deposited in an ionized oxygen medium, Journal of Vacuum Science and Technology A 8 (1990) 3260–3264.

[5] H.S. Kim, D.C. Gilmer, S.A. Campbell, D.L. Polla, Leakage current and electrical breakdown in metal–organic chemical vapor deposited TiO_2 dielectrics on silicon substrates, Applied Physics Letters 69 (1996) 3860–3862.

[6] M.R. Golobostanfard, H. Abdizadeh, Effect of mixed solvent on structural, morphological, and optoelectrical properties of spin-coated TiO_2 thin films, Ceramics International 38 (2012) 5843–5851.

[7] D.J. Kim, S.H. Hahn, S.H. Oh, E.J. Kim, Influence of calcination temperature on structural and optical properties of TiO_2 thin films prepared by sol–gel dip coating, Materials Letters 57 (2002) 355–360.

[8] H.W. Chen, K.C. Huang, C.Y. Hsu, C.Y. Lin, J.G. Chen, C.P. Lee, L.Y. Lin, R. Vittal, K.C. Ho, Electrophoretic deposition of TiO_2 film on titanium foil for a flexible dye-sensitized solar cell, Electrochimica Acta 56 (2011) 7991–7998.

[9] A. Chávez-Valdez, M. Herrmann, A.R. Boccaccini, Alternating current electrophoretic deposition (EPD) of TiO_2 nanoparticles in aqueous suspensions, Journal of Colloid and Interface Science 375 (2012) 102–105.

[10] M.J. Santillán, N.E. Quaranta, A.R. Boccaccini, Titania and titania–silver nanocomposite coatings grown by electrophoretic deposition from aqueous suspensions, Surface and Coatings Technology 205 (2010) 2562–2571.

[11] S. Lebrette, C. Pagnoux, P. Abelard, Fabrication of titania dense layers by electrophoretic deposition in aqueous media, Journal of the European Ceramic Society 26 (2006) 2727–2734.

[12] Y. Sun, I. Zhitomirsky, Electrophoretic deposition of titanium dioxide using organic acids as charging additives, Materials Letters 73 (2012) 190–193.

[13] W. Jarernboon, S. Pimanpang, S. Maensiri, E. Swatsitang, V. Amornkitbamrung, Optimization of titanium dioxide film prepared by electrophoretic deposition for dye-sensitized solar cell application, Thin Solid Films 517 (2009) 4663–4667.

[14] L. Mohan, D. Durgalakshmi, M. Geetha, T.S.N. Sankara Narayanan, R. Asokamani, Electrophoretic deposition of nanocomposite (HAp $+TiO_2$) on titanium alloy for biomedical applications, Ceramics International 38 (2012) 3435–3443.

[15] L. Besra, M. Liu, A review on fundamentals and applications of electrophoretic deposition (EPD), Progress in Materials Science 52 (2007) 1–61.

[16] O. Van Der Biest, S. Put, G. Anne, J. Vleugels, Electrophoretic deposition for coatings and free standing objects, Journal of Materials Science 39 (2004) 779–785.

[17] Y. Wang, G. Cao, Li^+-intercalation electrochemical/electrochromic properties of vanadium pentoxide films by sol electrophoretic deposition, Electrochimica Acta 51 (2006) 4865–4872.

[18] K. Hasegawa, S. Kunugi, M. Tatsumisago, T. Minami, Preparation of thick films by electrophoretic deposition using surface modified silica particles derived from sol–gel method, Journal of Sol–Gel Science and Technology 15 (1999) 243–249.

[19] L. Zhang, J. Zhai, W. Mo, X. Yao, The dielectric and leakage current behavior of $CoFe_2O_4$–$BaTiO_3$ composite films prepared by combining method of sol–gel and electrophoretic deposition, Solid State Sciences 12 (2010) 509–514.

[20] Y. Castro, A. Duran, R. Moreno, B. Ferrari, Thick sol–gel coatings produced by electrophoretic deposition, Advanced Materials 14 (2002) 505–508.

[21] H.C. Hamaker, Formation of a deposit by electrophoresis, Transactions of the Faraday Society 35 (1940) 279–287.

[22] J. Livage, M. Henry, C. Sanchez, Sol–gel chemistry of transaction metal oxides, Progress in Solid State Chemistry 18 (1988) 259–341.