Study on growth rate of TiO$_2$ nanostructured thin films: simulation by molecular dynamics approach and modeling by artificial neural network

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ABSTRACT: Effects of the deposition process parameters on the thickness of TiO$_2$ nanostructured film were simulated using the molecular dynamics (MD) approach and modeled by the artificial neural network (ANN) and regression method. Accordingly, TiO$_2$ nanostructured film was prepared experimentally with the sol–gel dip-coating method. Structural instabilities can be expected, due to short- and/or long-range intermolecular forces, leading to the surface inhomogeneities. In the MD simulation, the Morse potential function was used for the inter-atomic interactions, and equations of motion for atoms were solved by Verlet algorithm. The effect of the withdrawal velocity, drying temperature and number of deposited layers were studied in order to characterize the film thickness. The results of MD simulations are reasonably consistent with atomic force microscopy, scanning electron microscopy and Dektak surface profiler. Finally, the outputs from experimental data were analyzed by using the ANN in order to investigate the effects of deposition process parameters on the film thickness. In this case, various architectures have been checked using 75% of experimental data for training of the ANN. Among the various architectures, feed-forward back-propagation network with trainer training algorithm was found as the best architecture. Based on the R-squared value, the ANN is better than the regression model in predicting the film thickness. The statistical analysis for those results was then used to verify the fitness of the complex process model. Based on the results, this modeling methodology can explain the characteristics of the TiO$_2$ nanostructured thin film and growth mechanism varying with process conditions. © 2013 The Authors. Surface and Interface Analysis published by John Wiley & Sons Ltd.

Keywords: TiO$_2$ nanostructured thin film; growth rate; molecular dynamics simulation; artificial neural network; regression analysis

Introduction

TiO$_2$ nano-sized particles have attracted a significant interest of materials scientists and physicists due to their special properties. This material has attained a great importance in several technological applications such as solar cells,$^{[1-3]}$ photo-catalyst$^{[4]}$ sensors$^{[5-7]}$ and memory devices.$^{[8]}$ TiO$_2$ nanostructured thin films are also used as various optical coatings for its good transmittance in the visible region, high refractive index and chemical stability.$^{[9,10]}$

In the last two decades, several experimental methods, such as chemical vapor deposition,$^{[11]}$ pulsed laser deposition,$^{[12]}$ sputtering$^{[13]}$ and sol–gel technique, were used for preparation of the TiO$_2$ nanostructured films.$^{[14-16]}$ In comparison with other methods, the sol–gel technique has some advantages such as controllability, reliability and reproducibility. It can be selected for preparation of nanostructured thin films. Sol–gel coating is classified as two distinct methods named as spin and dip coating. The dip coating has been applied for preparation of TiO$_2$ nanostructured films. Experimental results have shown that preparation of high transparent TiO$_2$ nanostructured film by dip-coating method necessitates the control of film thickness and surface roughness.$^{[14]}$

In recent years, computer simulation methods have been used for the study of thin film structures. In particular, molecular dynamics (MD) simulations have been used to study of the impact of single cluster over the solid surface. MD simulations of materials at the atomic level are becoming an important technique for investigation of the configuration of crystals, melting and crystallization phenomena, phase transitions, diffusion and thermodynamic properties of inorganic materials.$^{[17-19]}$ The MD simulation procedure is conceptually simple; an arbitrary assemblage of N atoms or molecules (approximately several hundreds or thousands of atoms or molecules) confined to a specific region of space is considered. The periodic boundary conditions are used to generate an infinite system. The atoms and molecules are given some initial positions and velocities. Time development of the system is then solved by means of the Newtonian equations of motion for each time step of $10^{-16}$ to $10^{-14}$ s. The essential point in the MD simulation of materials is the description of the atomic interactions in terms of an interaction potential. It is well known that the accuracy of the potential function essentially contributes to the quality of the simulation results. Matsui and Akaogi carried out MD simulations to reproduce the structure and physical properties of TiO$_2$ particles.$^{[20]}$ The inter-atomic

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The potential function used in their work was composed of Columbic, van der Waals and Gilbert-type repulsion terms. They reported on reproducing or predicting a wide range of TiO₂ morphological properties. Fukuda et al. performed MD simulations of rutile phase using the Morse potential instead of the van der Waals interaction term.

In the past few years, several methodologies for the modeling of nonlinear characteristics that affect the surface morphology of thin film have been studied. Due to the complexity and nonlinear relationships in the system, modeling methodology using artificial intelligence, such as artificial neural network (ANN), has been developed to analyze the processes difficult to characterize by classical modeling methods. ANN has a wide variety of applications from banking to engineering. These applications may have more than one input and/or output. ANN can perform the highly complex mapping between input variables and output responses to establish nonlinear input–output relationships. In addition, neural network (NNet) can cover many aspects of functional relationships using a limited number of processing data.

Han and May performed NNet for the process modeling and analyzed the various conditions on the predicted model via genetic algorithms. Tripllett, May and Brown applied NNet to a device manufacturing process. Ko et al. investigated the process modeling of ZnO thin films grown by pulsed laser deposition using NNet based on the back-propagation (BP) algorithm. They used optimal experimental design technique and examined two operating factors, that is, temperature and pressure, to characterize the growth rate of ZnO thin film.

Hongyi et al. used ANN with BP algorithm to predict the diameter and length of the TiO₂ nanotube. In addition, BP ANN was applied to estimate average particle size of TiO₂ nanoparticles. Khanmohammadi et al. applied a novel technique based on diffuse reflectance near-infrared spectrometry and BP ANN for size estimation of TiO₂ nanoparticles. They show that the ANN is capable of generalizing and predicting the average size of nanoparticles.

In this study, TiO₂ nanostructured thin films were investigated from three viewpoints: experimental work with sol–gel dip-coating method, computer simulation using MD approach and modeling using ANN. It was shown that the results of MD simulations provide a good level of consistency with atomic force microscopy (AFM) and scanning electron microscopy (SEM) images regarding the morphology and surface structure of prepared films, respectively. Finally, the outputs from experimental data and MD simulations were analyzed by using the ANN and regression model in order to investigate the effects of deposition process parameters on the film thickness. Based on the ANN modeling results, this method can explain the characteristics of the TiO₂ nanostructured thin film and its growth mechanism as a function of process conditions.

**Experimental procedure**

TiO₂ nanostructured films were prepared by the hydrolysis of titanium tetra-ISOPOXIDE (TTIP) (Aldrich, 99.99%), which is generally used for TiO₂ nanostructured films by the sol–gel method. This method can employ a colloidal inorganic sol precursor using metal salts. The chemical composition of the sol matrix was TTIP: EtOH: H₂O: HNO₃ with 1:10:18:0.1 in molar ratio. The sol matrix was prepared at room temperature by mixing TTIP with absolute ethanol (Aldrich, 99.9%) and nitric acid (Aldrich, 99.9%) as a catalyst. More details of the solution preparation and their characterization can be found in our last paper. The TiO₂ nanostructured films were obtained by immersion of ultrasonically well-cleaned soda lime glass as a substrate into precursor solution by dip-coating method. The withdrawal velocity of substrate was varied from 2 × 10⁻⁴ to 1 × 10⁻³ Å/ns in 2 × 10⁻⁴ Å/ns intervals.

For heat treatment, each wet sample was inserted in the oven under vacuum condition at drying temperatures ranging from 623 to 823 K in 100 K intervals for 60 min.

![Figure 1. Structure of a neural network.](image1)

![Figure 2. Schematic diagram of calculation in a network with BP algorithm: (a) prediction stage and first part of weight optimization process; (b) second part of weight optimization.](image2)
The surface morphologies of the TiO₂ nanostructured films were characterized by AFM (DME DS-95-50) and SEM (Cam Scan MV2300) techniques. The film thickness was measured using Dektak surface profiler (Talystep IIA).

### MD simulation

MD simulations have been used to study the TiO₂ nanostructure film over a solid surface. The approach of atomistic simulation is based on the approximation of quantum interactions by classical ones. Instead of solving the Schrödinger equation, a semi-empirical model of classical interaction between atoms is constructed, and then the Newton equations are solved. In this study, before the reaction probabilities are studied on the TiO₂ layer, the substrate has to be brought to the minimum energy configuration. For this, the forces on the atoms in the system were calculated by taking the first derivative of the potential. From the forces, the new positions are obtained by solving the Newtonian equations of motions. If the potential energy of the new structure is greater than the previous one, the velocity of all atoms is set to zero, and the process is repeated until the potential energy attains a minimum. In order to describe the inter-atomic interactions of TiO₂ nanostructure films, Morse potential function has been used. The coefficients for Ti–O, Ti–Ti and O–O interactions applied in this function are represented in Appendix A.

The MD simulations were performed based on the LAMMPS code, which is intended for massively parallel and large-scale atomic/molecular simulations, developed at Sandia National Laboratories. LAMMPS integrates Newton’s equations of motion for atoms, molecules or macroscopic particles that interact via short- or long-range forces with a variety of initial and/or boundary conditions. The MD simulations applied in this work are fully dynamical with three-dimensional calculations in a simulation cell. The results of simulation were obtained for number of 8000 TiO₂ molecules. These numbers of TiO₂ molecules were corresponding to five-deposited layer in the experiments. A layer of atoms on each side of the substrate also forms boundary atoms. In the present simulation, the Verlet algorithm was used for the motion of atoms in the simulation cell. Ti–O bonds were located about 20 Å average distances from substrate in the simulation space. TiO₂ molecules were moved towards the surface with $2 \times 10^{-3}$, $2 \times 10^{-4}$, $1 \times 10^{-5}$ Å/ns velocity. Each simulation time and time step were 5 ns and 2 ps, respectively. The total simulation time required for a system with formation of TiO₂ layer was approximately 48 h on a PC with a 3.2 GHz Pentium 4 CPU.

#### Table 1. Summary of process parameters

| Factor                        | Symbol | Value | Remark   |
|-------------------------------|--------|-------|----------|
| Withdrawal velocity           | $\nu$ (Å/ns) | $2 \times 10^{-4}$ | Controllable |
| Drying temperature            | $T$ (K) | 623–823 | Controllable |
| Number of deposited layer     | $N$ (-) | 2–10 | Controllable |
| Mean thickness of film        | $h_{avg}$ (nm) | 19.9–174 | |

#### Figure 3. SEM images of TiO₂ nanostructured film prepared at 623 K with two levels of withdrawal velocity of (a) $1.0 \times 10^{-3}$ and (b) $2.0 \times 10^{-4}$ Å/ns.

#### Figure 4. SEM images of TiO₂ nanostructured with withdrawal velocity of $6.0 \times 10^{-4}$ Å/ns, at different drying temperatures of (a) 623 and (b) 723 K.
Modeling scheme

ANN

An ANN is a computational simulation of a biological NNet. A NNet consists of complex units that, in turn, are demonstrative of neurons of the body. The units are in the shape of a conjunct loop structure that, in fact, functions like axons and dendrites. A NNet learns by determining the relation between the inputs and outputs. By calculating the relative importance of the inputs and outputs, the system can determine such relationships. One example of the layered networks is provided in Fig. 1.

In Fig. 1, ANN input, hidden and output layers are shown. In this network, each pair of lines is interconnected via a weight. The two important features of NNet are swift response to problems and the ability of generalization of these responses to unobserved samples.\(^\text{32–34}\) One type of the well-known NNets is the feed-forward network, which is utilized to classify and estimate problems. In the feed-forward network, the signal travels only from input to output. The ANN selected in this work is a feed-forward BP network. According to Fig. 2, the learning sample set is presented to the network, and a BP algorithm automatically adjusts the weights; therefore, the output response to input vector is as close as possible to the desired response (Fig. 2 a). Each time a prediction is made, the result is compared to the corresponding desired value. Then, the prediction error (the difference between the predicted and real outputs) was BP across the network in a manner that allowed the interconnection weights to be modified according to the scheme specified by the learning rule (Fig. 2 b).\(^\text{35,36}\)

Prediction error can be used by improvement technique to teach NNet. Three performance functions, including of mean square error (MSE), root MSE (RMSE) and sum of square error (SSE), were studied in this work, which are described in Appendix B (Eqns B.2–4). As for the number of neurons needed in the hidden layer, it is desirable to have the least number of neurons possible so as to avoid overfitting problem. Cross-validation technique provides a useful way to circumvent the problem. This technique provides an estimate of model predictivity by comparing the predictive sum of squares against the sum of squared deviations of each network output,\(^\text{37,38}\) which is described in Appendix B (Eqn B.5).

Briefly, training process is a way from input layer to output layer in order to compute outputs and a backward route to correct weights. This process continues until the error is minimized. As soon as errors were minimized, the teaching process terminates.\(^\text{28,29,36}\) In order to characterize the dip-coating method, the range of process variables, which were considered as input factors of interest, is summarized in Table 1.

Multiple regression

Regression method is one of the most commonly used statistical techniques to obtain the relation between different output variables and input parameters.\(^\text{39,40}\) In order to analyze the variation of the output response, multi-variable linear regression method was carried out using SPSS software based on the experimental data. In this study, the regressed equation was obtained by using the three deposition process parameters as independent
variables (inputs) and the film thickness as dependent variable (output). The mathematical expression of multi-variable linear regression is described in Appendix C.

Results and discussion

TiO₂ nanostructured thin films were investigated from three viewpoints: experimental work with sol–gel dip-coating method, computer simulation using MD approach and modeling using ANN. The results of each section are presented in the following.

Experimental results

Figure 3 shows the SEM image of TiO₂ nanostructured film at drying temperatures of (a) 623 K, (b) 723 K and (c) 823 K.

Figure 6. Dektak surface profiler of prepared TiO₂ film at drying temperatures of (a) 623 K, (b) 723 K and (c) 823 K.

Figure 7. MD simulation results for surface profile of 8000 TiO₂ molecules at deposition rate of (a) $2 \times 10^{-7}$, (b) $6 \times 10^{-7}$ and (c) $1 \times 10^{-3} \text{Å}/\text{ns}$. [$h_{avg}$ is simulated mean height of the film]

velocity (Fig. 3 b) results in the bigger particle size with the dimensions of 24.61–40.37 nm.

Figure 4 shows the SEM image of TiO₂ nanostructured film with withdrawal velocity of $6.0 \times 10^{-4} \text{Å}/\text{ns}$ at two drying temperatures of 623 (Fig. 4 a) and 723 K (Fig. 4 b). It can be seen that, lower drying temperature (Fig. 4 a) induces the smaller particle size with the dimensions of 18.00–25.99 nm, while higher drying temperature (Fig. 4 b) induces the bigger particle size with dimension of 23.44–38.07 nm.

Figure 5 shows the AFM image of TiO₂ nanostructured film at drying temperature of 623 K with different levels of withdrawal velocity of $1.0 \times 10^{-3}$ (Fig. 5 a) and $2.0 \times 10^{-3} \text{Å}/\text{ns}$ (Fig. 5 b), when five layers were deposited on the substrate. It can be seen that lower withdrawal velocity (Fig. 5 b) induces the smaller particle size with the dimensions of 17.58–28.95 nm, while higher withdrawal velocity (Fig. 5 a) results in the bigger particle size with the dimensions of 24.61–40.37 nm.
during the films formation. The dark grooves observed in the AFM images may suggest the presence of cracks; however, the height profile indicates that the grooves are relatively superficial. As indicated, the depths associated with the deepest grooves (for example 25.1 nm in Fig. 5 a) are still much smaller than the film thickness (240 nm). Comparison of the AFM images indicates that the mean height of the film increased from 19.9 (Fig. 5 a) to 24.3 (Fig. 5 b), and then to 30.5 nm (Fig. 5 c), when the withdrawal velocity of samples increased from $2.0 \times 10^{-4}$ to $6.0 \times 10^{-4}$ and then to $1.0 \times 10^{-3}$ Å/ns, respectively.

Figure 6 illustrates the variation in the height of the summits as determined by the Dektak surface profiler for the prepared TiO$_2$ film at drying temperatures of 623 (Fig. 6 a), 723 (Fig. 6 b) and 823 K (Fig. 6 c) when two layers deposited on the substrate. The Dektak analysis shows that the surface morphology of TiO$_2$ film is transformed from the relatively homogenous surface with some height variation at 623 K depicted in Fig. 6 a to an aggregated structure exhibiting non-uniform morphology of the film thickness at 823 K shown in Fig. 6 c.

**Table 2.** Experimental design of dip-coating process as neural network variables

| Run | Withdrawal velocity (Å/ns) | Drying temperature (K) | Number of layer | Film thickness (nm) | Remark |
|-----|-----------------------------|------------------------|-----------------|---------------------|--------|
| 1   | $2 \times 10^{-4}$          | 623                    | 2               | 19.9                | TR     |
| 2   | $4 \times 10^{-4}$          | 623                    | 2               | 21.7                | TR     |
| 3   | $6 \times 10^{-4}$          | 623                    | 2               | 24.3                | TE     |
| 4   | $8 \times 10^{-4}$          | 623                    | 2               | 27.4                | TR     |
| 5   | $10^{-3}$                   | 623                    | 2               | 30.5                | TR     |
| 6   | $2 \times 10^{-4}$          | 723                    | 5               | 57.5                | TR     |
| 7   | $4 \times 10^{-4}$          | 723                    | 5               | 59.6                | TR     |
| 8   | $6 \times 10^{-4}$          | 723                    | 5               | 63.5                | TE     |
| 9   | $8 \times 10^{-4}$          | 723                    | 5               | 70.5                | TR     |
| 10  | $10^{-3}$                   | 723                    | 5               | 75                  | TR     |
| 11  | $2 \times 10^{-4}$          | 623                    | 10              | 114                 | TR     |
| 12  | $2 \times 10^{-4}$          | 723                    | 10              | 133.2               | TR     |
| 13  | $4 \times 10^{-4}$          | 723                    | 10              | 136.2               | TR     |
| 14  | $6 \times 10^{-4}$          | 723                    | 10              | 140                 | TE     |
| 15  | $8 \times 10^{-4}$          | 723                    | 10              | 142.1               | TR     |
| 16  | $2 \times 10^{-4}$          | 823                    | 10              | 143                 | TR     |
| 17  | $10^{-3}$                   | 723                    | 10              | 155.1               | TR     |
| 18  | $1 \times 10^{-3}$          | 823                    | 10              | 174                 | TR     |

TR: Training data TE: Testing data

**Figure 9.** Mean square error for tested data versus number of neurons in the hidden layer.

**Figure 10.** The cross-validation MSE plotted against the number of neurons in the hidden layer.

**MD simulation results**

Figure 7 represents the results of MD simulation for surface profile of 8000 TiO$_2$ molecules after 5 ns under three deposition rate of $2 \times 10^{-4}$, $6 \times 10^{-4}$ and $1 \times 10^{-3}$ Å/ns. These numbers of TiO$_2$ molecules were corresponding to five deposited layers in the experiments. It was shown that Ti–O bonds attached to
bridging oxygen due to cluster–cluster aggregation. The rapid cluster growth took place through the aggregation of such small clusters. The morphology demonstrated that cavities and voids were formed within the formation of the film and finally the structure of the simulated film became dense and packed with TiO₂ molecules.

MD simulation results show that with increase of deposition rate from $2 \times 10^{-4}$ (Fig. 7a) to $6 \times 10^{-4}$ (Fig. 7b) and then to $1 \times 10^{-3}$ Å/ns (Fig. 7c), the simulated mean height of the film increased from about 56 nm to 62 nm and then to 75 nm, respectively. Observing the surface profile, we concluded that at the lower deposition rate (Fig. 7a), the probability of local clustering in free space of the simulation cell was low, thus provided an insufficient number of atoms to yield a uniformly dense simulated film. At the higher deposition rates (Fig. 7c), the local clustering of the incident atoms took place in free space of the simulation cell to yield a dense film with relatively high local clustering in the surface. Increase of local clustering of the atoms led to surface inhomogeneities in the simulated film. The results of Fig. 7 agree with comparison of the experimental data obtained for film thickness and surface morphology using AFM image when five layers of TiO₂ were deposited on the substrate by dip-coating method.

Figure 8 represents the results of MD simulation for surface profile of 8000 TiO₂ molecules after 5 ns at two drying temperatures of 623 (Fig. 8a) and 723 K (Fig. 8b). It can be found from MD simulation that with an increase in the simulated drying temperature from 623 to 723 K, the mean height of the simulated film increased from about 61 to 69 nm, respectively. The MD simulated results of Figs. 7 agree with the film thickness obtained by Dektak surface profiler when five layers of TiO₂ were deposited on the substrate.

Results of ANN modeling

In this study, we have used feed-forward BP network with Bayesian Regularization as a training function. The network was trained on 15 experimental runs, and the rest of data was used to test generalization capacity of the network. Table 2 illustrates the experimental design of dip-coating process factors used in each run as NNet variables.

In order to analyze the deviation and the variation of the ANN output, each performance function was calculated. As for the number of neurons needed in the hidden layer, it is desirable to have the least number of neurons possible so as to avoid the overfitting problem. The minimum number of neurons in this work was obtained from the testing MSE and cross-validation MSE plotted versus the number of neurons in the hidden layer. In Fig. 9, MSE for the tested data is plotted as a function of the number of neurons in the hidden layer. The plot shows the MSE value for networks of different sizes starting from one hidden neuron up to 50. Figure 9 also depicted that for the architecture with 25 neurons, we get the minimum MSE value. The
network architecture with 25 neurons into the hidden layer was considered as optimal for this application. During the training phase, the weights and biases which are the parameters of the ANN model are adjusted so that the network outputs fit the experimental data. Therefore, we selected a network with 25 neurons which has a little error with a fast computation time. The best ANN obtained in this study is a one hidden layer feed-forward BP network with 25 neurons, as indicated in Fig. 9.

To verify the number of neurons selected by the testing MSE, the cross-validation MSE versus the number of neurons in the hidden layer is plotted in Fig. 10. As can be seen, the cross-validation MSE decreases rapidly at first and then levels out but continues to approach the minimum value (about 0.1) as the number of neurons increases to 25. Subsequently, the MSE value starts to increase gradually again when the number of neurons increases to 50.

The transfer function of the first layer is hyperbolic tangent sigmoid, and that of the second layer is linear function. For this network, the predicted values versus measured values are shown in Fig. 12. It can be seen that there is a perfect match between experimental data and ANN output. The plot of residuals versus fitted values is shown in Fig. 12. It can be seen that the residuals are randomly distributed around zero, and no special pattern is observed.

The $R^2$ value represents the proportion of variation in the response explained by the model. The $R^2$ values of ANN and regression model are 0.994 and 0.903, respectively. Therefore, the portion of the model explained by ANN is better than that of regression model in predicting the film thickness of nanostructured thin films.

Table 3 shows the experimental data, ANN outputs (film thickness) and percent of error for the best network with 25 neurons in the hidden layer. The differences between experimental and predicted film thickness are less than 1.0%. This network can approximately be generalized to all sorts of data because the differences between predicted and measured value are diminutive, which proves the capability of ANN to predict unobserved data correctly. The values of MSE, RMSE and SSE obtained by the regression and ANN models are shown in Table 4.

The 3D plot of surface response for the film thickness when numbers of 10 layers of TiO$_2$ film were deposited on the substrate is shown in Fig. 13. It is observed that the thickness of the TiO$_2$ film is near the maximum value when the drying temperature is in the range of 723 to 823 K and the withdrawal velocity is in the range of $8 \times 10^{-4}$ to $1 \times 10^{-3}$ Å/ns. It can be found that, when withdrawal velocity and drying temperature increase, the growth rate and, as a result, mean thickness of film increase. The ANN model suggested in this study can be in good agreement with the growth rate related to the characteristics of TiO$_2$ nanoparticles such as SEM image and X-ray diffraction.$^{[30]}$

The main purpose for the use of ANN in this study is that it operates in series to the MD simulation. It also performs a multitude of activities such as prediction, data reconciliation and reduction of processing time. This means that the use of ANN model combining with MD simulated data results in the reduction of number of experiments. NNNet is found to be very efficient in terms of processing time and modeling error compared to the MD simulation. Of course, these methods must be compared on fair basis, namely computer speed and system memory. Overall simulation process is supervised by comparing the experimental results and MD outputs. Figure 14 shows the block diagram in the case of combining ANN method and MD simulation of thin film fabrication for a real system.

**Conclusion**

The characterization of the growth rate of TiO$_2$ nanostructured thin film prepared with the sol–gel dip-coating method has been investigated. At first, effects of deposition process parameters, such as withdrawal velocity, drying temperature and number of deposited layers on the thickness of the prepared film, were experimentally investigated. Experiments showed that the withdrawal velocity played a major role in the prepared film thickness. MD simulation considering Morse potential function simulations has been employed to study the morphology of the TiO$_2$ nanostructured film. The simulation results showed that with increase in withdrawal velocity, the mean height of the simulated film increased. In addition, at the low deposition rate, the probability of local clustering in free space of the simulation cell was low, and due to cluster–cluster aggregation, a uniformly packed and dense simulated film was obtained. MD simulations reveal that with increase of simulated temperature, the mean height of the simulated film increased. Moreover, in this study,
the results of MD simulation, in the cases of change in withdrawal velocity and drying temperature, were compared with the SEM, AFM and Dektak surface profiler, and there was good agreement between the simulated results and experimental data. Finally, the film growth mechanism of the dip-coating method was well explained by the NNet model in order to investigate the effects of deposition process parameters on the film thickness. In this case, various architectures have been checked using 75% of experimental data for training of ANN. Among the various architectures, feed-forward BP network with trainer training algorithm was found as the best architecture. Although the effects of deposition processing parameters were complex, the output responses were reasonably estimated by the proposed NNet model. Based on the modeling results, the ANN was more accurate model than the regression model, indicating that the ANN model is able to predict in complex system such as film deposition processing. Therefore, this methodology can be used to improve the manufacturability of the nanostructured thin films.

**Notations**

\[ \text{Å} \] angstrom  \\
avg average  \\
C cut-off distance  \\
D bond strength  \\
h height  \\
M measure  \\
N number of experiments  \\
P predict  \\
r radius  \\
\[ R^2 \] regression  \\
s second  \\
T temperature  \\
v displacement velocity

**Abbreviations**

ANN artificial neural network;  
BP back-propagation;  
MD molecular dynamics;  
MSE mean square error;  
NNet neural network;  
RMSE root mean square error;  
SSE sum of square error

**References**

[1] P. P. Boix, Y. H. Lee, F. Fabregat-Santiago, S. H. Im, I. Mora-Sero, J. Bisquert, S. I. Seok, ACS Nano, 2012, 6, 873.  
[2] W. Tan, J. Zhang, Y. Weng, Z. Shuai, X. Xiao, X. Zhou, X. Li, Y. Lin, Surf. Interface Anal. 2007, 39, 809.  
[3] W-P. Liao, S-C. Hsu, W-H. Lin, J-J. Wu, J. Phys. Chem. C, 2012, 15, 15938.  
[4] T. Aartti, G. Madras, Ind. Eng. Chem. Res., 2007, 46, 7.  
[5] N. O. Savage, S. A. Akbar, P. K. Dutta, Sens. Actuators B, 2001, 72, 239.  
[6] J. Chapman, F. Regan, Adv. Eng. Mat., 2012, 14, 175.  
[7] C. Wang, L. Yin, L. Zhang, Y. Qi, N. Lun, N. Liu, Langmuir, 2010, 26, 12841.  
[8] C. Lee, I. Kim, W. Choi, H. Shin, J. Cho, Langmuir, 2009, 25, 4274.  
[9] B. S. Richards, Prog. Photovoltaics: Res. Appl. 2004, 12, 253.  
[10] Y. Cai, M. Liu, AIChE J. 2012, 58, 1907.  
[11] M. Kemell, V. Pore, M. Ritala, M. Leskelä, M. Lindén, J. Am. Chem. Soc., 2005, 127, 14178.  
[12] M. Terashima, N. Inoue, S. Kashiwabara, R. Fujimoto, Appl. Surf. Sci., 2001, 169, 535.  
[13] B. Okolo, P. Lamparter, U. Welzel, T. Wagner, E.J. Mittemeijer, Thin Solid Films 2005, 474, 50.  
[14] M. Sasani Ghamarsi, A. Bahramian, Mat. Lett., 2008, 62, 361.  
[15] P. Kajitvichyanukul, J. Ananpattarachai, S. Pongpoom, Sci. Technol. Adv. Mat. 2005, 6, 352.  
[16] N. Venkatachalam, M. Palanichamy, and V. Murugesan, J. Mater. Chem. Phys. 2007, 104, 454.  
[17] R. Webb, M. Kerford, E. Ali, M. Dunn, L. Knowles, K. Lee, J. Mistry, F. Whitefoot, Surf. Interface Anal. 2001, 31, 297.  
[18] D. Huang, J. Pu, Z. Lu, Q. Xue, Surf. Interface Anal. 2012, 44, 837.  
[19] L. F. Drummy, P. K. Miska, D. Alberts, N. Lee, D. C. Martin, J. Phys. Chem. B, 2006, 110, 6066.  
[20] M. Matsui, M. Akaogi, J. Mol. Simul. 1991, 6, 239.  
[21] K. Fukuda, I. Fuji, R. Kitoh, Acta Crystallogr. 1993, 849, 781.  
[22] P. M. Morse, Phys. Rev. 1929, 34, 57.  
[23] J. Card, A. L. Testoni, L. A. L. Tarte, Surf. Interface Anal. 1995, 23, 495.  
[24] T. Yang, Y-A. Shen, Comp. Ind. Eng. 2011, 60, 769.  
[25] M. A. Boyacioglu, Y. Kara, Ö. K. Baykan, Exp. Sys. Appl. 2009, 36, 3355.  
[26] W. Sha, Appl. Therm. Eng. 2007, 27, 688.  
[27] S-S. Han, G. S. May, IEEE Trans. Semicond. Manufacturing. 1997, 10, 279.  
[28] G. Triplet, G. S. May, A. Brown, Solid State Elec., 2002, 46, 1519.  
[29] Y-D. Ko, P. Moon, C. E. Kim, M-H. Ham, J-M. Myoung, I. Yun, Exp. Sys. Appl. 2009, 36, 4061.  
[30] M. Khanmohammadi, A. B. Garmarudi, N. Khoddami, K. Shabani, M. Khanlari, Microchem. J., 2010, 95, 337.  
[31] A. J. Markworth, Mater. Lett. 1984, 2, 333.  
[32] A. B. Blusari, Neural Networks for Chemical Engineers, Elsevier science Press, Amsterdam, 1995.  
[33] B. Joseph, F. H. Wang, P. S. Shieh, Comp Chem. Eng. 1992, 16, 413.  
[34] MATLAB, Neural Network Toolbox, The MathWorks Inc, 2007.  
[35] J. S. Torrecilla, M. L. Mena, P. Yanez-sedeno, J. Garcia, J. Agric. Food Chem., 2007, 55, 7418.  
[36] H. Zhang, J. Zhao, Y. Jia, X. Xu, C. Tang, Y. Li, Exp. Sys. Appl. 2012, 39, 4094.  
[37] A. Vieira, N. P. Barradas, C. Jeynes, Surf. Interface Anal. 2001, 31, 35.  
[38] R. Sentiono, Neural Comput. 2001, 13, 2865.  
[39] H-T. Pao, Exp. Sys. Appl. 2008, 35, 720.  
[40] A. M. Zain, H. Haron, S. N. Qasem, S. Sharif, Appl. Math. Model. 2012, 36, 1477.

**Appendix A**

The Morse potential function consists of two exponential terms as follows:

\[
u(r_{ij}) = D \left( \exp[-\alpha(r_{ij} - r_0)] - 2 \exp[-\alpha(r_{ij} - r_0)] \right) r_{ij}, \
\]

where \(D\) (eV) is related to the bond strength, \(r_0\) (Å) is the equilibrium inter-atomic separation, \(\alpha (\text{Å}^{-1})\) is related to the curvature at the potential minimum and \(r_{ij}\) is the cut-off distance. The Morse potential coefficients \(\alpha\) for Ti–O, Ti–Ti and O–O interactions are represented in Table A.1.

**Table A.1.** The Morse potential parameters for Ti–O, Ti–Ti and O–O interactions \(\alpha\) for Ti–O, Ti–Ti and O–O interactions

| Interaction   | \(D\) (eV) | \(\alpha\) (Å\(^{-1}\)) | \(r_0\) (Å) |
|---------------|-----------|---------------------|-------------|
| Ti–O          | 1.0279493 | 3.640737            | 1.88265     |
| Ti–Ti         | 0.00567139| 1.5543              | 4.18784     |
| O–O           | 0.042117  | 1.1861              | 3.70366     |

**Appendix B**

Functions of errors studied in this work are represented as follows:
Mean square error (MSE)

\[ \text{MSE} = \frac{1}{N} \sum_{i=1}^{N} (P_i - M_i)^2 \]  

(2)

Root mean square error (RMSE)

\[ \text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (P_i - M_i)^2} \]  

(3)

Sum of square error (SSE)

\[ \text{SSE} = \sum_{i=1}^{N} (P_i - M_i)^2 \]  

(4)

where \( P_i, M_i \) and \( N \) are the \( i \)th predicted model output, \( i \)th measured output and the number of samples, respectively.

Cross validation is:

\[ R^2 = 1 - \frac{\sum (P_i - M_i)^2}{\sum (M_i - \bar{M})^2} \]  

(5)

where \( \bar{M} \) is the mean value of measured output.

**Appendix C**

The mathematical expression of multi-variable linear regression model is summarized as follows:

\[ y^* = \alpha_1 x_1 + \alpha_2 x_2 + \ldots + \alpha_k x_k + \epsilon \]  

(6)

where \( y^* \) is a response variable, \( x_i \)'s are the process variables, \( \alpha_i \)'s are regression coefficients estimated using the ordinary least squares method and \( \epsilon \) is a modeling error.

The minimized SSE is:

\[ \text{SSE} = \sum_{i=1}^{n} (y_i - y^*)^2 \]  

(7)

\[ = \sum_{i=1}^{n} (y_i - \alpha_1 x_1 - \alpha_2 x_2 - \ldots - \alpha_k x_k + \epsilon)^2 \]  

(8)

for \( k \geq 2 \).

The relationship among each SSE and the notations is the following form:

\[ \text{SSE} = \text{SST}-\text{SSR} \]  

(9)

where SST is total sum of squares:

\[ \text{SST} = \sum_{i=1}^{n} (y_i - \bar{y})^2 \]  

(10)

SSR is sum of squares due to regression:

\[ \text{SSR} = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \]  

(11)

where \( \bar{y} \) and \( \hat{y}_i \) are mean and fitted value, respectively.

The \( R^2 \) value can be expressed in the following form:

\[ R^2 = \frac{\text{SSR}}{\text{SST}} = 1 - \frac{\text{SSE}}{\text{SST}} \]  

(12)