Modelling of titanium oxynitride films for decorative coating by using response surface methodology

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Abstract. In this work, titanium oxynitride films were deposited on SS316L and Si-wafer substrates using reactive DC magnetron sputtering. An experimental design and statistical analysis were applied for the thin film coating. The experiment software (Design-Expert Software) was used to design the deposition parameters, including the plasma current density (10-25 mA/cm²) and N₂ gas flow rate (20–60 sccm) by maintaining O₂ gas flow rate. Response surface methodology based on a central composite design was used to empirically model the influence of the plasma current density (I) and N₂ (N) flow rate on the CIE colour system of titanium oxynitride thin films. The model fitting equations for two colour channels (a* and b*) were obtained and represented by

\[ a^* = -26.65 + 0.67N + 2.92I + 0.02NI - 0.01N^2 - 0.12I^2 \]

\[ b^* = 4.83 - 1.05N + 1.72I - 0.02NI + 0.02N^2 - 0.03I^2 \]

In addition, the effects of current density and N₂ flow rate on the chemical composition of TiON films were investigated by X-ray photoelectron spectroscopy (XPS). The titanium 2p (Ti²p) spectra indicated that the TiON and TiO₂ structures depended on the deposition parameters. Additionally, the increase in N₂ flow rate and current density affected the increase of the TiN structure. Cytotoxicity was performed on the Ti sheet and the TiON film on SS316L by assessing the cellular response to L929 fibroblast cells. The result shows that the TiON film on SS316L exhibits good biocompatibility with the L929 fibroblast cells.

Keywords: titanium oxynitride, RSM, colour control, decoration, biocompatibility

1. Introduction

The continuous progress in thin film technology is largely connected to the adjustment of structural and chemical properties of the films to actual applications. Transition metal oxynitride films represent a particular class of materials that possess the superior properties of oxides (colours, optical properties, chemical stability) and nitrides (hardness and resistance) (Rizzo et al., 2009; Banakh et al., 2014; Do et al., 2014; Subramanian et al., 2011; Barhai et al., 2010). Titanium oxynitride coloured film is attractive due to its consumer demands in the decoration and ornament industries for its variety of colours, such as gold, blue, pink and green (Barhai et al., 2010). These films have been prepared by various chemical and physical deposition techniques, but the mass production of coloured films at short intervals is a challenging task for this industry (Barhai et al., 2010).
DC magnetron sputtering deposition is the most widely used technique industrially due to its possibility of large-scale fabrication of high-quality films (Gingley, 2010). Indeed, a good understanding of the reactive sputtering process is essential when tailoring the film properties. Understanding the basic growth process that involves all the possible phenomena leading to oxynitride formation is significant for determining the fundamental mechanism that explains the composition. A growth model of titanium oxynitride based on Berg’s model was proposed by Rizzo et al. The results show that filling nitrogen vacancies by reactions with oxygen atoms is favoured in the formation of titanium oxynitride films. In addition, the literature indicates that the colours of the titanium oxynitride film mostly depend on the film thickness and the oxide-to-nitride ratio during deposition (Barhai et al., 2010; Braic et al., 2007; Jeyachandran et al., 2007). A very careful control of gas flow rates is needed to prepare this film. Barhai et al. reported that the oxygen content in the films was controlled by varying the current density (Barhai et al., 2010).

However, the fundamentals of growth mechanisms are very complicated for applications in the decoration and ornament industries. In this work, empirical modelling of titanium oxynitride colours by using response surface methodology (RSM) was proposed and used to connect the fundamental research to its actual application. Titanium oxynitride thin films were deposited on SS316L and Si substrates at room temperature using DC reactive magnetron sputtering technique. RSM was used for a statistical study of the effects of deposition parameters, including the plasma current density (10–25 mA/cm²) and N₂ gas flow rate (20–60 sccm) on the colours of films. The standard CIE-LAB colour model was used in this work. In addition, cytotoxic effects (assays based on cell cultures) were employed on the thin films.

2. Materials and Methods

2.1 Experimental Design
RSM based on a central composite design (CCD) was used to design the deposition parameters of titanium oxynitride films. The effects of the deposition parameters, including the plasma current density represented by I (range of 10–25 mA/cm²) and the N₂ gas flow rate represented by N (range of 20–60 sccm) kept under a constant O₂ gas flow rate, on the colour were investigated. The experimental design and statistical analysis were achieved by the Design-Expert Software v.9.0.3 (StatEase, Minneapolis, USA) and the analysis of variance (ANOVA), respectively. The experimental design with the responses (a*, b*) is shown in Table 1.

2.2 Preparation of Films
In this work, titanium oxynitride films were deposited on stainless steel (316L) and Si-wafer substrates using reactive DC magnetron sputtering. SS316L substrates of 3×3 cm² in size were obtained by laser cutting and were sequentially grounded with sand paper numbers 600, 1,000, 2,000 and 4,000. Then, they were polished with monocrystalline diamond suspensions with particle sizes of 3 µm and 0.1 µm. After that they were cleaned with chemical solutions such as trichloroethylene, acetone, and methanol in an ultrasonic bath; they were rinsed with deionized water and then blow-dried with N₂ gas at room temperature prior to deposition. The vacuum system was evacuated below 6.0 x 10⁻⁶ mbar by a diffusion pump. The high purity (99.99%) of the Ti target with 3-inch diameters and ultra-high purities (99.9995%) of argon (Ar), nitrogen (N₂) and oxygen (O₂) gases were used in the deposition system. A pre-sputtering process with Ar at 100 W for 20 min was employed to avoid contamination prior to deposition. During deposition, the total argon and nitrogen flow rate (Ar + N₂) was maintained at 100 sccm, and the oxygen gas flow rate was kept at 2.5 sccm. Three different mass flow controllers were used to regulate each gas flow. The thicknesses of the titanium oxynitride thin films under different conditions were controlled to approximately 0.5 µm using a quartz crystal microbalance located near the substrate holder.
2.3 Measurements and Characterization

Chemical structures and elemental compositions

The chemical natures of the outermost parts of the films were obtained by X-ray photoelectron spectroscopy (XPS) using the AXIS Ultra DLD instrument. The XPS measurements were performed using AlKα (X-ray of 1486.6 eV source). XPS peak fitting/deconvolution and peak areas estimation were analysed for the chemical structure of each film and its Ti, N and O contents.

2.4 CIE-LAB Colour

Photographs of the deposited samples were taken by digital camera and shown in Fig. 1. Sample areas of 5x5 mm² were analysed with a spatial resolution of 12 mm/pixel. The colour specification under the standard CIE illuminant D65 was computed and represented in the CIELAB 1976 colour space for each individual pixel in the area. The colour space was defined by the CIE based on one channel for Luminance (lightness) (L) and two colour channels (a* and b*). In this model, the perceived colour differences correspond to distances when measured colourimetrically. The a* axis extends from green (-a*) to red (+a*), and the b* axis extends from blue (-b*) to yellow (+b*).

2.5 Cytotoxic effects

Cytotoxicity was studied by assessing the cellular response to L929 fibroblast cells. Mouse fibroblast cells (L929, ATCC, USA) were cultured in culture flasks with Dulbecco’s Minimum Essential Medium supplemented with 10% foetal bovine serum and incubated at 37 °C and 5% CO₂ under humidified conditions. Cells were subcultured to 24 well plates using a Trypsin–EDTA solution and allowed to form a monolayer. Once the cells attained confluency, test samples were kept in contact with cells, and a cytotoxicity test based on ISO-10993-5 was performed. Materials after exposure to platelet-rich plasma (PRP) for 30 min were rinsed thoroughly with phosphate-buffered saline and fixed with 2% glutaraldehyde overnight. They were then rinsed and dehydrated with a graded concentration of ethyl alcohol. The samples were critical point dried, gold sputter coated and viewed under the scanning electron microscope (SEM; EVO-MA10).

3. Results and Discussion

Fig. 1 shows the various TiON film colours on SS316L substrates obtained from a total of 13 experimental designs. The photographs were taken using a digital camera with a dimension of 3x3 cm². By considering the design of the experiments, 8 experiments had different deposition parameters (Run number: 1, 2, 3, 5, 7, 8, 11, and 13) while 5 had similar deposition parameters (Run number: 4, 6, 9, 10, and 12). The films with the same deposition parameter showed the same colour. This result indicated that the experiment was reproducible. The quantitative results show that the current density and N₂ flow...
rate affect the film colours. In addition, the experiments show the reliability of deposition parameter controls. The quantitative analysis of film colours were analysed based on the standard CIE-LAB.

3.1 Model Fitting and Statistical Analysis

| Run number | Factors  | Responses |
|------------|----------|-----------|
|             | N₂ flow rate (sccm) | Current density (mA/cm²) | a* | b* |
| 1          | 11.7     | 17.5      | -1.1 | 10.1 |
| 2          | 68.3     | 17.5      | -13.3 | 13.8 |
| 3          | 20.0     | 25.0      | -15.0 | -1.5 |
| 4          | 40.0     | 17.5      | 4.6  | -3.1 |
| 5          | 20.0     | 10.0      | 1.0  | 5.1  |
| 6          | 40.0     | 17.5      | 4.6  | -3.0 |
| 7          | 60.0     | 10.0      | -6.6 | 11.3 |
| 8          | 40.0     | 6.9       | -3.9 | -9.2 |
| 9          | 40.0     | 17.5      | 4.5  | -3.0 |
| 10         | 40.0     | 17.5      | 4.5  | -3.1 |
| 11         | 60.0     | 25.0      | -10.8 | -8.2 |
| 12         | 40.0     | 17.5      | 4.6  | -3.2 |
| 13         | 40.0     | 28.1      | -15.2 | -3.5 |

Statistical analysis was performed by ANOVA using experimental data obtained in Table 1. The significance of the model fit of the experimental data was determined by parameters F test, p value, R-squared and lack of fit (Noshadi et al., 2012). The F value is the ratio of the model mean square to the residual mean square and is used as the test statistic for comparing model variance with residual variance (Gül Boyaci San et al., 2013). The F value must be used in combination with the p value to test the significance of the model. Generally, the tested models showed the model and the coefficient terms are statistically significant when the p value is <0.05 (Gül Boyaci San et al., 2013).
Table 2. ANOVA of the model for the $a^*$

| Source    | Sum of Squares | F-value | p-value Prob> F |
|-----------|----------------|---------|-----------------|
| Model     | 751.41         | 39.28   | < 0.0001 significant |
| A-N       | 53.32          | 13.94   | 0.0073          |
| B-I       | 163.63         | 42.77   | 0.0003          |
| AB        | 34.81          | 9.10    | 0.0195          |
| A$^2$     | 229.90         | 60.10   | 0.0001          |
| B$^2$     | 333.48         | 87.17   | < 0.0001 significant |
| Lack of Fit | 26.77        | 2974.03 | < 0.0001 significant |
| Pure Error | 0.012         |         |                 |

R-Squared ($R^2$) = 0.9656, Adj R-Squared = 0.9410

The analysis of variance (ANOVA) of the model for the $a^*$ is shown in Table 2. The model F-value of 39.28 implies that the model is significant. There is only a 0.01% chance that an F-value this large could be caused by noise. Values of “Prob> F” less than 0.0500 indicate model terms that are significant. In this case, parameters A ($N_2$ gas flow rate, N), B (current density, I), AB, A$^2$ and B$^2$ are significant model terms (values greater than 0.1000 indicate the model terms are not significant). The efficiency of the model was investigated by comparing the performance of lack of fit. The lack of fit F-value of 2974.03 implies the lack of fit is significant relative to pure error. There is only a 0.01% chance that an F-value this large could be caused by noise. $R^2$ and the adjusted determination coefficient of R$^2$ are both greater than 0.85, indicating that this is a good statistical model (Reddey et al., 2008). Three-dimensional and contour plots showing the effects of the N and I on the $a^*$ are shown in Fig. 2(a) and (b), respectively. It can be observed that the $a^*$ value of the TiON thin film tended to be a negative value with a $N_2$ gas flow rate greater than 50 sccm or a current density higher than 19 mA/cm$^2$. The regression equation for the $a^*$ was fit using a second order polynomial model, as shown in Eq. (1):

$$a^* = -26.65 + 0.67(N) + 2.92(I) + 0.02(NI) - 0.01(N^2) - 0.12(I^2)$$

Figure 2. (a) Surface curve and (b) contour plots of the $a^*$ value of the TiON thin film.
The ANOVA for the model of b* is shown in Table 3. The model F-value of 4.73 implies that the model is significant. However, the lack of fit F-value was 9944.26, implying that the lack of fit is significant relative to pure error. The adjusted determination coefficient (adjusted R² = 0.8541) was also high, implying that the model has high significance. The regression model developed for the b* can be plotted as response surface and contour plots, as shown in Fig. 3. The b* was a negative value (blue colour) when the current density was higher than 22 mA/cm² and the N₂ flow rate was in the range of 30-50 sccm. The regression equation for the b* was fit using a second order polynomial model, as shown in Eq. (2):

Table 3. ANOVA of the model for the b*

| Source    | Sum of Squares | F-value | p-value | Prob> F |
|-----------|----------------|---------|---------|---------|
| Model     | 506.19         | 4.73    | 0.0330  | significant |
| A-N       | 3.04           | 0.14    | 0.7173  |          |
| B-I       | 40.09          | 1.87    | 0.2133  |          |
| AB        | 40.32          | 1.88    | 0.2122  |          |
| A^2       | 366.07         | 17.11   | 0.0044  |          |
| B^2       | 24.68          | 1.15    | 0.3185  |          |
| Lack of Fit | 149.76       | 9944.26 | < 0.0001 | significant |
| Pure Error | 0.020         |         |         |          |

R-Squared (R²) = 0.9018, Adj R-Squared = 0.8541

Figure 3. (a) Surface curve and (b) contour plots of the b* value of the TiON thin film.
\[
b^* = 4.83 - 1.05(N) + 1.72(I) - 0.02(NI) - 0.02(N^2) - 0.03(I^2)
\]  

(2)

3.2 XPS Analysis

Analyses of the chemical structure and elemental compositions of all TiON films were investigated by X-ray photoelectron spectroscopy (XPS). The four selective samples with different deposition parameters (current density and N\textsubscript{2} gas flow rate) were presented. The titanium 2p (Ti\textsuperscript{2p}) core level spectra of the samples are shown in Fig. 4. The spectra show two main peaks at binding energies of 458.8 eV and 464.5 eV corresponding to the TiON and TiO\textsubscript{2} structures, respectively (Barhai et al., 2010; Braic et al., 2007). The intensity of TiO\textsubscript{2} was at the same level in each sample while that of TiON depended on the deposition parameters. It may be due to the constant O\textsubscript{2} flow rate and the variation of N\textsubscript{2} flow rate.

![Figure 4. The titanium 2p (Ti\textsuperscript{2p}) core level spectra of four samples under different conditions: (a) N\textsubscript{2} = 20 sccm/I = 25 mA/cm\textsuperscript{2}, (b) N\textsubscript{2} = 20 sccm/I = 10 mA/cm\textsuperscript{2}, (c) N\textsubscript{2} = 60 sccm/I = 10 mA/cm\textsuperscript{2}, and (d) N\textsubscript{2} = 60 sccm/I = 25 mA/cm\textsuperscript{2}.](image)

The nitrogen 1s (N\textsuperscript{1s}) core level spectra of each different sample are shown in Fig. 5. The significant peak at 396.8 eV corresponds to the TiN structure (Kim et al., 1996). However, this peak shows a silent feature and almost no signature in Fig. 5(b). This indicates that more of the TiN structure is deposited on the film at both high N\textsubscript{2} flow rate and current density. Since the enthalpy of formation of TiO\textsubscript{2} (\(\Delta H_f = -944 \text{ kJ/mol}\)) is much less than that of TiN (\(\Delta H_f = -338 \text{ kJ/mol}\)) (Martin et al., 2001; Lu et al., 2004), TiO\textsubscript{2} should be more easily formed than TiN at standard conditions.

In addition, a broad peak is observed (ranging from 398 to 405 eV) for all the samples. This peak was deconvoluted and fitted to two peaks at binding energies of 399.2 eV and 402.4 eV. The first peak was associated with the TiON phase (Kim et al., 1996). Greczynski et al. (2016) reported that a new broad peak form at 402.4 eV due to interstitially incorporated molecular nitrogen. TiO\textsubscript{2} formation results in a release of molecular N\textsubscript{2} according to the reaction TiN + O\textsubscript{2} \rightarrow TiO\textsubscript{2} + \(\frac{1}{2}\)(N\textsubscript{2}) (Esaka et al., 1997; Greczynski et al., 2016).
Figure 5. Nitrogen 1s (N\textsuperscript{1s}) core level spectra of four samples under different conditions: (a) N\textsubscript{2} = 20 sccm/ I = 25 mA/cm\textsuperscript{2}, (b) N\textsubscript{2} = 20 sccm/ I = 10 mA/cm\textsuperscript{2}, (c) N\textsubscript{2} = 60 sccm/ I = 10 mA/cm\textsuperscript{2}, and (d) N\textsubscript{2} = 60 sccm/ I = 25 mA/cm\textsuperscript{2}.

3.3 Effect of current density

Figure 6. Elemental compositions of TiON films as a function of current density: (a) oxygen (b) nitrogen and (c) titanium contents (unit in %).
The effects of current density on elemental composition (Ti:N:O) are described in this section. In Fig. 6a, the O content increases as the current density increases for the low N\textsubscript{2} gas flow rate (20 sccm). This result is consistent with Barhai et al. (2010) and was expected since higher current density signifies more ionization of the oxygen atoms in the plasma. The ratio of N\textsubscript{2} and O\textsubscript{2} flow rate was 12:1 in the work of Barhai et al. (2010) while the ratio is approximately 8:1 in this study. When the N\textsubscript{2} flow rate was increased to 40 and 60 sccm, it also increased the nitrogen content with the decrease of oxygen content. The increase of N\textsubscript{2} flow rate enhanced the reaction of nitrogen with titanium. The N content of TiON films slightly increases as the current density increased for the low N\textsubscript{2} gas flow rate (20 sccm), as shown in Fig. 6b. When the N\textsubscript{2} gas flow rate increases, the current density appeared more effective in increasing the N content. It may cause the increase of ionization of nitrogen-species due to increasing plasma current density. In Fig. 6c, the Ti content increases with increasing current density for all the different N\textsubscript{2} flow rates. It causes the increase of the amount and kinetic energy of sputtering ions, which bombard the Ti target and gain more Ti atoms dropped from the target to the substrate. In addition, a major portion of the film has a composition corresponding to titanium oxide.

3.4 Effect of N\textsubscript{2} flow rate

![Graphs showing elemental composition of TiON films as a function of N\textsubscript{2} flow rate](image)

**Figure 7.** Elemental compositions of TiON films as a function of N\textsubscript{2} flow rate: (a) oxygen (b) nitrogen and (c) titanium contents (unit in at.%).

Fig. 7a and 7b show the corresponding increase of N content and decrease of O content with increasing N\textsubscript{2} flow rate. The O\textsubscript{2} gas flow rate was kept constant at lower rate (2.5 sccm) while the N\textsubscript{2} flow rate was varied between 10 to 70 sccm. Nitrogen is a reactive gas, but it has a lower reaction compared to oxygen. The increase of N\textsubscript{2} gas increased the probability of nitrogen to react with titanium and then form the TiN and/or TiON structures into the films. The N\textsubscript{2} flow rate is an important parameter
to control the chemical composition. However, the N\textsubscript{2} flow rate in the range of 20-60 sccm has a slight influence on the Ti content, as seen in Fig. 7c. The current density has greater dominance than the N\textsubscript{2} gas flow rate for Ti content.

3.5 Cytotoxic Test

![SEM micrographs of Ti sheet and TiON film](image)

**Figure 8.** Typical SEM micrographs of the L929 fibroblast cells on a (a) Ti sheet and (b) TiON film coated on SS316L.

SEM images of titanium and a TiON film on SS316L substrates attached with L929 fibroblast cells are shown in Fig. 8(a) and 8(b). The TiON film did not show any cytotoxic reaction in comparison with the titanium substrate when the films were kept in contact with fibroblast cells. The amount of cells on the TiON film is more than the amount on the titanium substrate, indicating good biocompatibility. Cytotoxicity studies revealed that all these coatings passed the test; hence, the coatings could be classified as non-cytotoxic material and have a potential for industrial decorative coating applications.

4. Conclusions

In conclusion, the colours of TiON thin films were investigated under various current densities and N\textsubscript{2} flow rates using the response surface methodology technique. The statistical analysis shows the significance of the model fit of the experimental data. Our study resulted in four conclusions:

1. It can be observed that the a* value of TiON thin films tended to be a negative value with a N\textsubscript{2} gas flow rate greater than 50 sccm or a current density higher than 19 mA/cm\textsuperscript{2}.
2. It can be observed that the b* value of TiON thin films tended to be a negative value with a N\textsubscript{2} gas flow rate in the range of 30-55 sccm or a current density higher than 20 mA/cm\textsuperscript{2}.
3. The high current density directly affects the Ti content while the ratio of N\textsubscript{2} to O\textsubscripts{2} flow rate affects the O and N contents in the films.
4. The cytotoxic test indicated the good biocompatibility of TiON films.

Acknowledgements

This work was supported by The Gem and Jewelry Institute of Thailand (Public organization) and the National Research Council of Thailand.

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