

Formation of TiO₂ thin films by a modified sol-gel route and characterization of structural, optical and electrochromic properties

Fatma Pınar Gökdemir¹, vecihe Ece Yüzbaşıoğlu¹, Bahadır Keskin², Orhan Özdemir^{1*}, Kubilay Kutlu¹

¹Department of Physics, Yıldız Technical University, Esenler, Istanbul, Turkey

²Department of Chemistry, Yıldız Technical University, Esenler, Istanbul, Turkey

*Corresponding author. Tel: (+90) 2123834248; E-mail: pinargokdemir1984@gmail.com

Received: 26 August 2013, Revised: 29 September 2013 and Accepted: 18 October 2013

ABSTRACT

Through a modified sol gel route with titanium isopropoxide (TIP) and acetic acid, titanium dioxide (TiO₂) thin films were deposited by dip coating. Employing acetic acid as modifier and without inclusion of water in hydrolysis led to control the degree of condensation-oligomerization of the precursor and formation of anatase phase only upon annealing. Direct allowed energy band gap 3.87 eV verified the anatase phase of the film. Impact of temperature on structural properties was deduced by FTIR and UV-Visible spectroscopies. Due to the reduction in band gap with increase in annealing temperature, injected Li⁺ charge amount dropped in anatase compared to the amorphous (unannealed) films. Copyright © 2014 VBRI press.

Keywords: Titanium dioxide; chelation effect; phase transformation; cathodic electrochromism.



Fatma Pınar Gökdemir was born in 1984 and graduated from Physics Department at Yıldız Technical University in 2006. She is a research assistant and phd student at the same university. Her research is focused on electrochromic materials, high K oxides and Li ion batteries.



Vecihe Ece Yüzbaşıoğlu was born in 1989. She graduated from Physics Department at Trakya University in 2011. She is a msc student at Yıldız Technical University and her thesis based on electrochromic properties of TiO₂ thin films.



Orhan Özdemir was born in 1973. He graduated from Physics Department at Middle East Technical University. Both msc and phd degree were taken from the same university. He is an Associated Professor Doctor at Yıldız Technical University and vice president of Physics Department. His current interest on electrochromism, transparent conducting oxides and silicon hetero-junction based solar cells.

Introduction

Titanium dioxide (TiO₂) is an environmental oxide that gained a great attention due to its interesting chemical, electrical and optical properties. These outstanding properties directly depend on the crystalline phase. Normally, TiO₂ exhibits polymorphs with three phases; anatase, rutile as tetragonal whereas brookite orthorhombic. While rutile phase is optically active and the most stable of these three; anatase phase has attracted much attention because of its higher photocatalytic activity for photocatalysis [1] and solar energy conversion [2,3]. Sol gel method is one of the best ways to fabricate TiO₂ films onto different substrates at low temperature with lower cost. Mostly, as deposited films exhibit amorphous phase and by thermal heat treatment phase transition occurs from amorphous to anatase phase around 500°C. However other deposition processes may cause anatase phase accompany by rutile and brookite traces. Amorphous to anatase phase transformation not only depends on annealing but also species that get involved in sol synthesis. TiO₂ sol preparation usually has three approaches; Ti alkoxide precursors in aqueous [4-6] or organic media [7], hydrolysis of TiCl₄ at low temperatures [8] and non-hydrolytic combination of Ti alkoxide and TiCl₄ [9].

In this work, impact of annealing temperature on TiO₂ films, produced by a modified sol-gel route, was studied. Moreover, due to advantage of the sol, annealing caused to formation only one phase (anatase) of TiO₂ film.

Furthermore, it was substantiated from the CV analysis that Li^+ charge amount dropped in anatase compared to the amorphous (unannealed) TiO_2 films. Such experimental finding was interpreted by quantum confinement effect and traced by variation of energy band gap with increase in annealing temperature.

Experimental

Materials and synthesis of coating sol

Titanium(IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 99.999% trace metals basis, Aldrich) was used as TiO_2 coating sol precursor. 9.3 ml of isopropyl alcohol (IPA, $\text{CH}_3)_2\text{CHOH}$, $\geq 99.7\%$, Aldrich) was added to 3.2 ml TIP solution and mixed at $70 \pm 10^\circ\text{C}$ on a magnetic stirrer. 10.3 ml acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 100% Puriss Glacial, Sigma Aldrich) introduced to the mixture as a chelating agent and stirred. After adding 24 ml methanol (CH_3OH , $\geq 99.5\%$, Merck) to this mixture solution transformed a white precipitate and dissolved in 25 ml methanol giving a translucent, moonstone colored solution.

Preparation of thin films

TiO_2 thin films were deposited on SLG (soda lime glass, ISO LAB) and ITO (Indium Tin Oxide coated glass, Resistivity 25-30 ohms/sq) substrates at room temperature by dip coating technique. Prior to deposition all substrates were cleaned in an ultrasonic bath at 30°C with acetone, isopropyl alcohol and deionized water, respectively. Dipping speed was constant at 100 mm/min and samples were dried at room temperature before heat treatment at 100°C for 20 min. Resuming the same processes for double layer, uniform and crack free films were produced. Finally films were annealed under air at different temperatures; 200°C , 300°C and 500°C for 1 h.

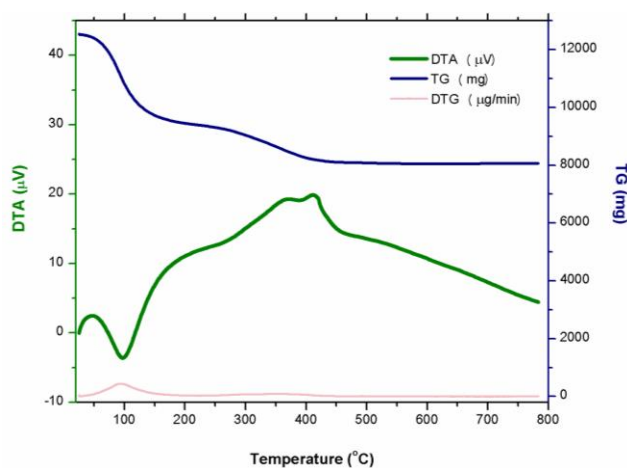


Fig. 1. TG DTA pattern of TiO_2 coating solution

Characterizations

Coating sol was dried in an open atmosphere at room temperature. The coating sol powder was used for thermogravimetric and differential thermal analyses (TG-DTA) prior to heat treatment. TG DTA measurements were performed with a Seiko SII Exstar 6300 model thermal analysis system using an alumina crucible in static air

ambient with a heating rate of $10^\circ\text{C}/\text{min}$. The structural properties of the films were investigated by means of Fourier transform infrared spectroscopy (FTIR) using a Bruker Tensor27 model IR spectrophotometer and measuring range was $200\text{--}4000\text{ cm}^{-1}$. Optical properties were examined with transmittance experiments in the range of $200\text{--}1100\text{ nm}$ using a PG Instruments T80 model UV Vis spectrophotometer. Surface morphology and particle size of the films were determined through atomic force microscopy (AFM) with a Park Systems operating at non-contact mode. Electrochemical analyses were carried out using cyclic voltammetry experiments with an Autolab PGSTAT30 potentiostat galvanostat in a conventional three-electrode electrochemical cell where a platinum and silver wire were used as a counter (CE) and reference electrode (RE), respectively. Experiments were performed in a 1 molar (M) lithium perchlorate propylene carbonate (LiClO_4/PC) electrolyte at the bias voltage between $+1\text{V}$ and -2.5V .

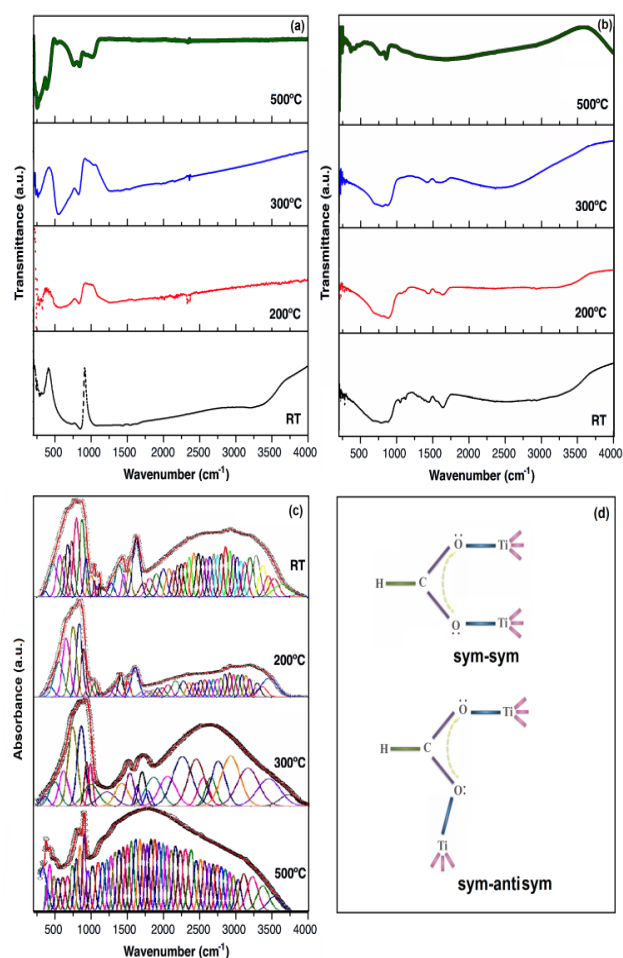


Fig. 2. Transmittance FTIR spectra of the films on (A) SLG, (B) ITO coated glass substrates with different annealing temperature. In (C), IR modes and corresponding bonds after the deconvolution process of the films onto ITO coated glass substrates. (D) shows a bridging mode of chelation of formate group for sym-sym and sym-antisym.

Results and discussion

TG-DTA analysis

TG-DTA pattern of the coating powder was given in Fig. 1. It showed two mass losses associated with endothermic and

exothermic events. The first endothermic event took place around 90°C, corresponded to the elimination of water while following exothermic events were due to the volatilization and combustion of other species such as CH₃OH, (CH₃)₂CHOH and CH₃COOH. Nearly localized two peaks in the DTA curve at 367°C and 410°C, were ascribed to the transition of the amorphous to anatase phase of the film. There were no associated signals demonstrating anatase-rutile phase transition between 400-800°C.

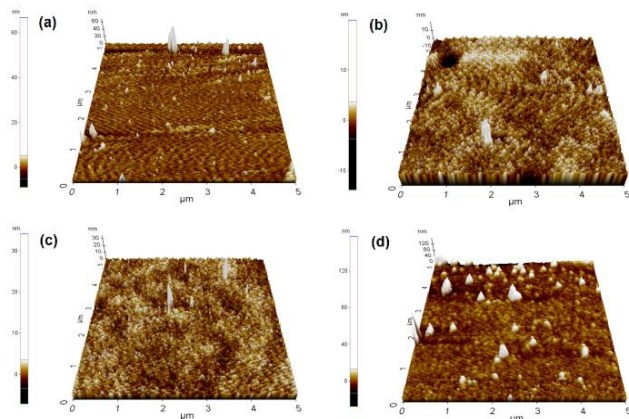


Fig. 3. AFM images of the films onto SLG substrates: as grown (A) and annealed at (B) 200°C (C) 300°C (D) 500°C, respectively.

FTIR spectroscopy

Raw transmittance FTIR spectra and their deconvolution results on absorbance curves were illustrated in **Fig. 2**. After the deconvolution process, IR modes and corresponding bonds for the present films were identified. The presence of Ti-O-Ti and Ti-O polymeric chains was clearly evident from the bands at 471 and 789 cm⁻¹. Also, vibration of the Ti-O-O band was identified from the band at 693 cm⁻¹ [10]. Moreover, the bands at 1009, 1122, and 1138 cm⁻¹ were ascribed to stretching of Ti-O-C [11] while LO mode of amorphous TiO₂ [12] appeared at 874 cm⁻¹.

The broadband from 3000 to 3600 cm⁻¹ associated with the stretching vibration modes of hydroxyl groups [13], began to broaden after the addition of water appeared at 1635 cm⁻¹. The bands appeared at 1288 and 1368 cm⁻¹ are the vibration mode of C-O-O group [14]. The doublet in 1441 and 1538 cm⁻¹ designated the symmetric and asymmetric stretching vibration of the carboxylic group coordinated to Ti as a bidentate ligand [15]. Moreover, the separation between these signals proposed that acetate behaves preferentially as a bidentate rather than as a bridging ligand between two Ti atoms [11-16] (**Fig. 2(d)**) since the latter possibility requires higher than 150 cm⁻¹. Upon annealing at 500°C, the bands at 366, 412, 517, 642, 754 cm⁻¹ confirmed the presence of anatase phase of the film. In other words, phase transition from amorphous to anatase phase took place under 500°C heat treatment.

Morphological investigation using AFM

AFM results of as deposited and annealed films were displayed in **Fig. 3**. As to the analysis, crack free and homogeneous films were synthesized. Moreover, as

annealed temperature increased, granule sizes were grown that were determined according to the analysis.

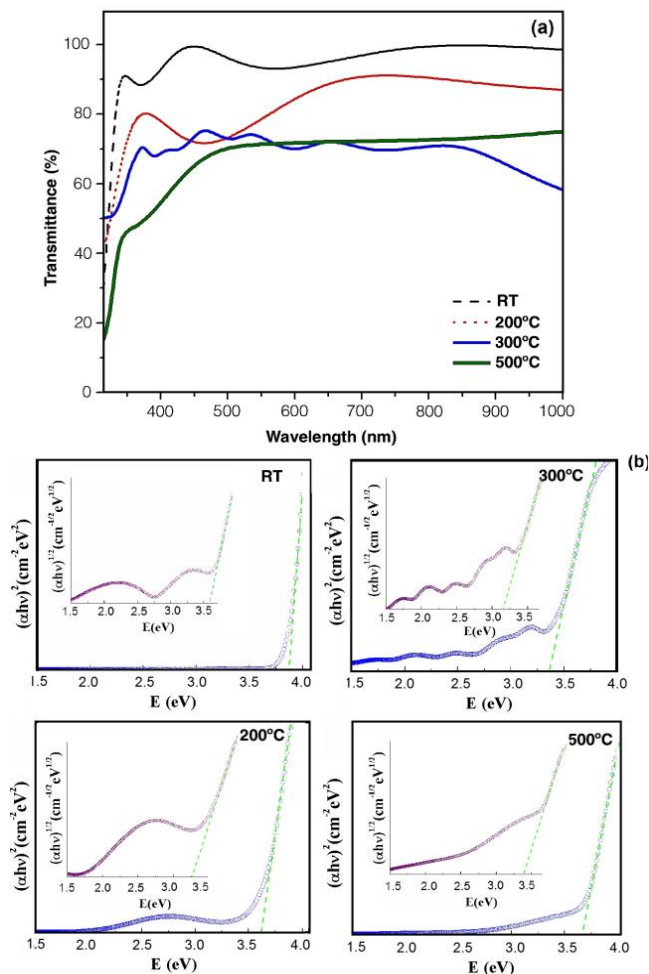


Fig. 4. (a) Optical transmittance spectra (b) Tauc plots of the films onto SLG substrates.

Optical Properties with UV Transmittance Analysis

Optical transmittance spectra of the films deposited on SLG substrates were given in **Fig. 4(a)**. Transmittance patterns exhibited that decrease in annealing temperature causes a red shift on the absorption edges. On the other hand, optical band gap were determined by Tauc plots using absorption coefficients [17]. According to Tauc's law,

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A was a constant, $h\nu$ was photon energy, E_g was optical energy band gap and n was the fingerprint of the transition. Cases of n=1/2, 3/2, 2 and 3 denoted direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. **Fig. 4(b)** showed that best fit for the films was given by a direct allowed transition and gap values varied as 3.87, 3.64, 3.36 and 3.68 eV for the as grown and heat treated at 200°C, 300°C and 500°C, respectively. On the contrary, indirect allowed band gap of the films were determined as 3.59, 3.10, 2.68 and 3.24 eV for the as grown and heat treated at 200°C, 300°C and 500°C, respectively. Taking into account of

reduction in particle size by decreasing in annealing temperature, such evidence could be interpreted as quantum size effect [18].

Cyclic voltammetry measurements

Titanium dioxide film showed cathodic electrochromism and its color changed from transparent to blue with the injection of electrons and Li^+ ions into the oxide matrix by a reaction given in relation (2). In there, variation of x from 0.5 to 1 was attributed to the transforming of anatase to amorphous phase [19-21],

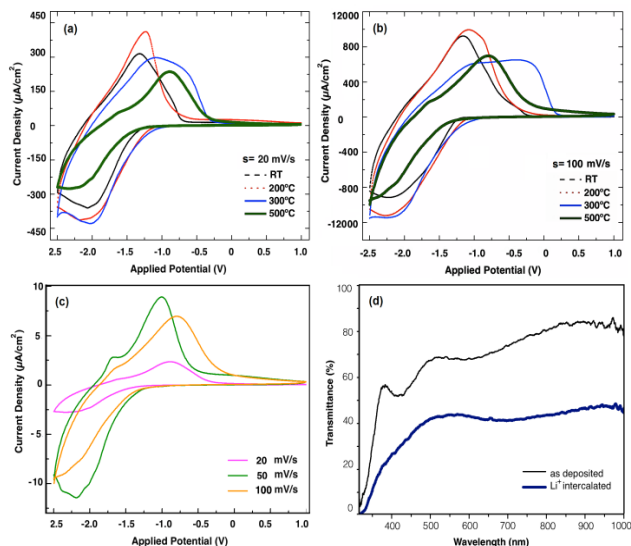
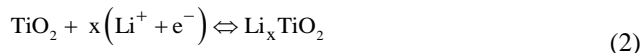


Fig. 5. Cyclic voltammograms of the films at (A) 20 mV/s, (B) 100 mV/s scan rates. Cyclic voltammograms (C) and transmittance spectra for bleached/lithiated states (D) of the annealed film at 500°C.

Cyclic voltammograms (CVs) of TiO_2 films were given in **Fig. 5**. Additionally, charge capacities of the films were calculated and given in **Table. 1** where inserted/extracted charge amount during coloration/bleaching $\text{Ti}^{4+} \leftrightarrow \text{Ti}^{3+}$ states denoted as ratio of charges (Q_c/Q_a) for the present films.

Table 1. Inserted/extracted charge capacities at 20 mV/s sweep rate in 1M LiClO_4/PC .

film	Q (mC/cm ²)				Q _c /Q _a
	cycle	2	3	4	
RT		17.8/13.3	17.4/13.2	17.0/13.1	16.5/13.0
200°C		21.6/15.8	23.4/15.8	24.7/16.2	27.1/17.0
300°C		23.3/16.9	23.0/16.8	22.7/16.7	22.3/16.7
500°C		14.3/10.6	13.7/10.4	13.5/10.3	13.0/10.3

It seemed that increasing in annealing temperature up to 500°C, TiO_2 films became more compact and charge capacities differed with a small increment. That might be originated from easier Li^+ insertion without undergoing two-phase transition from the tetragonal to orthorhombic phase, which causes internal stress in the crystalline anatase structure [22] for annealing temperatures lower than phase transition temperature. According to cyclic voltammograms, anodic peak positions of as deposited films were found to be much more negative than heat

treated ones, indicating much easier insertion of Li ions [23]. In-situ transmittance change of annealed TiO_2 thin film during lithium insertion was depicted in **Fig. 5(D)**. Optical density (ΔOD) and coloration efficiency (η) at a single wavelength (550 nm) were calculated using transmittance and the inserted charge amount [24, 25] as:

$$\Delta OD = \log \left(\frac{T_{\text{bleached}}}{T_{\text{colored}}} \right) \quad (3)$$

$$\eta = \frac{\Delta OD}{q} \quad (4)$$

The change in the optical density and coloration efficiency were found to be 0.19 and 13.97 cm^2/C , respectively.

Conclusion

Ex-situ heat treatment on as grown films had drastically impacted on both structural and electrochemical properties: due to the quantum confinement, energy band gap of the films began to decrease while granule size of the films started to grow. Upon a transition of amorphous to anatase phase in TiO_2 film around 500°C, charge capacity of the film dropped gradually.

Acknowledgements

This study is financially supported by Yildiz Technical University projects under a contract of 2012-01-01-DOP02 and 2011-01-01-KAP03. The authors thank to Assoc. Prof. Dr. Nevim SAM for FTIR measurements.

Reference

- Zhang, J.; Xu, Q.; Feng, Z.; Li, M.; Li, C.; *Angew. Chem. Int.*, **2008**, *47*, 1766.
DOI: [10.1002/anie.200704788](https://doi.org/10.1002/anie.200704788)
- Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A.; *Nano Lett.*, **2006**, *6*, 215.
DOI: [10.1021/nl052099j](https://doi.org/10.1021/nl052099j)
- Adachi, M.; Murata, Y.; Takao, J.; Jiu, J.; Sakamoto, M.; Wang, F.; *J. Am. Chem. Soc.*, **2004**, *126*, 14943.
DOI: [10.1021/ja048068s](https://doi.org/10.1021/ja048068s)
- Kumar, P.; Badrinarayanan, S.; Sastry, M.; *Thin Solid Films*, **2000**, *358*, 122.
DOI: [10.1080/03602550802189076](https://doi.org/10.1080/03602550802189076)
- Yoldas, B. E.; *J. Mater. Sci.*, **1986**, *21*, 1087.
DOI: [10.1007/BF01117399](https://doi.org/10.1007/BF01117399)
- Kotov, N.; Meldrum, F.; Fendler, J. H.; *J. Phys. Chem.*, **1994**, *98*, 8827..
DOI: [10.1021/j100087a002](https://doi.org/10.1021/j100087a002)
- Skinner, D. E.; Colombo, D. P.; Jr, Cavaleri, J. J.; Bowman, R. M.; *J. Phys. Chem.*, **1995**, *99*, 7853..
DOI: [10.1021/j100020a003](https://doi.org/10.1021/j100020a003)
- Serpone, N.; Lawless, D.; Khairutdinov, R.; *J. Phys. Chem.*, **1995**, *99*, 16646.
DOI: [10.1021/j100045a026](https://doi.org/10.1021/j100045a026)
- Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; A solution chemistry study of nonhydrolytic sol-gel routes to titania, Vioux, A.; *Chem. Mater.*, **1997**, *9*, 694-698.
DOI: [10.1021/cm960337t](https://doi.org/10.1021/cm960337t)
- Gao, Y.; Masuda, Y.; Peng, Z.; Yonezawa, T.; Koumoto, K.; *J. Mater. Chem.*, **2003**, *1*, 608.
DOI: [10.1039/b208681f](https://doi.org/10.1039/b208681f)
- Parra, R.; Góes, M. S.; Castro, M. S.; Longo, E.; Bueno, P. R.; Varela, J. A.; *Chemistry of Materials*, **2008**, *20*, 143.
DOI: [10.1021/cm702286e](https://doi.org/10.1021/cm702286e)
- Gonzalez R. J.; Zallen R.; Berger, H.; *Phys. Rev. B: Condens. Matter*, **1997**, *55*, 7014.
DOI: [10.1103/PhysRevB.55.7014](https://doi.org/10.1103/PhysRevB.55.7014)

13. Maira, A. J.; Coronado, J. M.; Augugliaro, V.; Yeung, K. L.; Conesa, J. C.; Soria, J.; *J. Catal.* **2001**, *202*, 413.
DOI: [10.1006/jcat.2001.3301](https://doi.org/10.1006/jcat.2001.3301)
14. Burgos, M.; Langlet, M.; *Thin Solid Films*, **1999**, *349*, 19.
PII: [S0040-6090\(99\)00139-X](https://doi.org/10.1016/S0040-6090(99)00139-X)
15. Nolan, N. T.; Seery, M. K.; Pillai, S. C.; *J. Phys. Chem. C*, **2009**, *113*, 16151.
DOI: [10.1021/jp904358g](https://doi.org/10.1021/jp904358g)
16. Uurlaub, R.; Posset, U.; Thull, R.; *J. Non-Crystalline Solids*, **2000**, *265*, 276.
PII: [S0022-3093\(00\)00003-X](https://doi.org/10.1016/S0022-3093(00)00003-X)
17. Tauc, J.; Abeles, F.; *Optical properties of solids*, **1972**, North-Holland, Amsterdam.
18. Akkaya, A. U. O.; Tepehan, F. Z.; *Surf. Coatings Technol.*, **2011**, *206*, 37.
DOI: [10.1016/j.surfcoat.2011.06.039](https://doi.org/10.1016/j.surfcoat.2011.06.039)
19. Tauc, J.; Abeles, F.; *Optical properties of solids*, **1972**, North-Holland, Amsterdam
20. Granqvist C. G.; *Handbook of Inorganic Electrochromic Materials*, **1995**, Elsevier, Amsterdam.
21. Dyer, C. K.; Leach, J. S. L.; *J. Electrochem. Soc.*, **1978**, *125*, 23.
DOI: [10.1149/1.2131391J](https://doi.org/10.1149/1.2131391J)
22. Ohtsuka, T.; Masuda, M.; Sato, N.; *J. Electrochem. Soc.*, **1987**, *134*, 2406.
DOI: [10.1149/1.2100212](https://doi.org/10.1149/1.2100212)
23. Ryu, W. H.; Nam, D. H.; Ko, Y. S.; Kim, R. H.; Kwon, H. S.; *Electrochim. Acta*, **2012**, *61*, 19.
DOI: [10.1016/j.electacta.2011.11.042](https://doi.org/10.1016/j.electacta.2011.11.042)
24. Wang, Z.; Hu, X.; *Thin Solid Films*, **1999**, *352*, 62.
PII: [S0040-6090\(99\)00321-1](https://doi.org/10.1016/S0040-6090(99)00321-1)
25. Bange, K.; Gambke, T.; *Adv. Mat.*, **1990**, *2*, 10.
DOI: [10.1002/adma.19900020103](https://doi.org/10.1002/adma.19900020103)
26. Wang, C. M.; Lin, S. Y.; *J. Solid State Electrochem.*, **2006**, *10*, 255.
DOI: [10.1007/s10008-005-0690-6](https://doi.org/10.1007/s10008-005-0690-6)

Advanced Materials Letters

Publish your article in this journal

[ADVANCED MATERIALS Letters](#) is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including [DOAJ](#) and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

