Research Paper

Improvement in Gasochromic Properties of Tungsten Trioxide by Optimized Pd Doping

Abstract

Tungsten oxide layers are important structures in Gasochromic and optical hydrogen sensing devices. In the present study, these layers are constructed using sol-gel method and covered on glass with spin coating method. In order to investigate the catalytic role of palladium on the surface of layer, palladium has been coated on WO_3 layers by the same method. This catalyst was coated on WO_3 layers in the form palladium chloride with different concentrations of palladium. These layers have been baked at different temperatures to study the gasochromic properties of WO_3 layer in different crystalline and amorphous phases. Their Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-Ray Diffraction (XRD) and spectrophotometer analysis have been conducted for investigating the surface morphology, structure of layers and the size of nanoparticles. After exposing the colored glass to air or oxygen pressure, the sensor has mostly re-obtained its initial transparency. According to the results obtained from XRD spectra, the layers commence crystallization at 300˚ C and become totally crystallized at 500˚ C. In this study, the effects of temperature and catalyst concentration are investigated simultaneously. The optimal conditions have been achieved at 300˚ C and 0.05M concentration of palladium chloride solution. In this condition, after applying 2.7% hydrogen gas, the transmission modulation (ΔT) of the sample has been obtained as 47% and response time as 3sec. ΔT and reverse time have been 22% and 25sec.,respectively,after applying 10 litr/min O_2 gas for 1min.

Keywords: WO_3, Thin film, Sol-gel, Nano particles, Gasochrome, Palladium, Hydrogen sensor.

1.INTRODUCTION

Gasochromic films consist of an electrochromic layer such as WO_3 and a very thin coating of a catalyst. At the surface of the catalyst, hydrogen gas is disaggregated to hydrogen atoms, which colorize the gasochromic films [1].These gasochromic devices are applied for optical modulation in large-area windows applications [2] as well as where hydrogen is used as fuel. Due to their simple layer structures [3], WO_3 is one of the most promising materials among the ones showing gasochromic properties [4]. An incremental interest is seen in using WO_3 gasochromic coloration due to its appropriate response to H_2 gas [5, 6].

Gasochromic specification depends mostly on the preparation methods of WO_3 films [7, 8]. Therefore sol-gel technique is the most promising method for preparing these films thanks to its advantages such as simple equipments and low costs [9, 10 and 11].

The electrons and ions are entered to or exited from gasochromic material in gasochromic process, based on the gas density, in such a way that the number of electric charges remains constant. This process is resulted in forming the optical absorption bands in active gasochromic materials.

In explaining the effect of gasochromic, it should be considered that the thin layers of tungsten oxide have WO_{3-x} stoichiometry, before receiving hydrogen gas and Oxygen vacancy. Therefore, annealing them is ended in absorbing oxygen on or filling the mentioned vacancies and converting their structural patterns to WO_3. After applying hydrogen and diffusing hydrogen atoms to the lattice, these atoms react with WO_3 and H_2O molecules and WO_2 lattice is formed. The transparency of the layer is also reduced because of WO_3 to WO_2 conversion [12, 13].

This is a reversible process; it means that whenever the colored films are exposed to O_2 gas, the reaction occurs reversely and the sensor achieves its initial transparency through WO_2 to WO_3 conversion [14].

The characteristic of Pd catalyst at the surface plays an important role in disintegrating of H_2 /O_2 molecules for speeding the coloration/bleaching of the glass.

Lin zhuang et al. (2003) have conducted similar test by adding $PdCl_2$ to WO_3 sol and covering glasses by dip coating method [15] and calculated the size of grain 50-60nm. They applied 5% H_2/Ar to the samples and reported the response and reverse times lower than 60s in the optimum condition.

Ranjbar et al. (2010) have been used PLD technique for WO_3 along with electroless plating for Pd. The rate of maximum coloring/bleaching has been obtained in the form of ΔOD in 820sec. under applying 10% H_2/Ar.

Comparing to the above experiments, 47% ΔT(near to ΔT in [15]) has been obtained in only 3sec. by applying 2.7% H_2 through a simpler and cheaper method(sol-gel and spin coating) and 10-20nm nanoparticles by kudo procedure [16].

While gasochromism phenomenon and therefore its relevant sensors work at room temperatures, other metal-oxide resistive sensors, are active only at the temperatures higher than 150˚ C. Lower temperature causes the reduction of power and energy consumption, increases the lifetime and stability of sensors. Therefore working at lower temperatures is the greatest advantage of gasochromic devices.

2. MATERIAL AND METHODS

In this study, sol-gel method has been used in order to construct WO_3 solution. In this regard, concerning the kudo method, 5gr tungsten metal powder (merck) is poured in 20ml hydrogen peroxide and stirred for a few hours to produce the milky colored peroxotungstic acid. This reaction is highly exothermic and the flask should necessarily be cooled to prevent the reactants from sudden spurting. The solution is heated at 60˚C for an hour to evaporate the extra H_2O_2. Then 10ml ethanol is added to the solution and heated at 80˚C for 20 minutes. Finally, a light yellow transparent solution is obtained which can be deposited on the glass after 24h.

Pd is also added to distilled water in the form of $PdCl_2$ powder (Merck), in order to synthesize the catalyst solution with different concentrations. Moreover, a few drops of HCl are added to the $H_2O +$ $PdCl_2$ solution to facilitate the dissolution process stirred for 4-5 hours, until obtaining a light brown solution without any palladium deposits. In this study, 3 different molarities of the solution (0.01M, 0.05M and 0.1M) have been made.

Spin coating method has been used for 25sec. with the speed of 2500 rpm for depositing WO_3 and Pd solutions on the glass in the form of thin films. Primary annealing has been performed on each sample at 70˚C for 10min.

The samples are exposed to 2.7% hydrogen gas and measured for their transparency changes. Then the colored films are flushed with 10 lit/min O_2 gas for 1min to meet 10% of their initial transmissions. Finally, the samples are exposed to the air to achieve their initial transmissions.

3. RESULTS AND DISCUSSION

TEM image of WO_3 solution is taken by Philips EM208 microscope at 100KV and presented in Figure1.

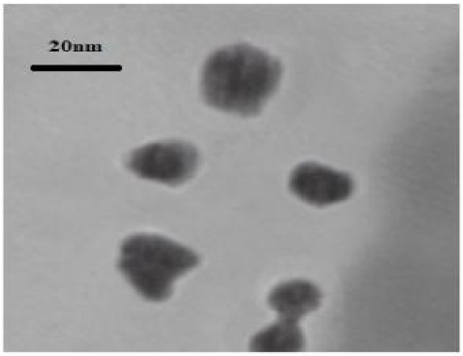
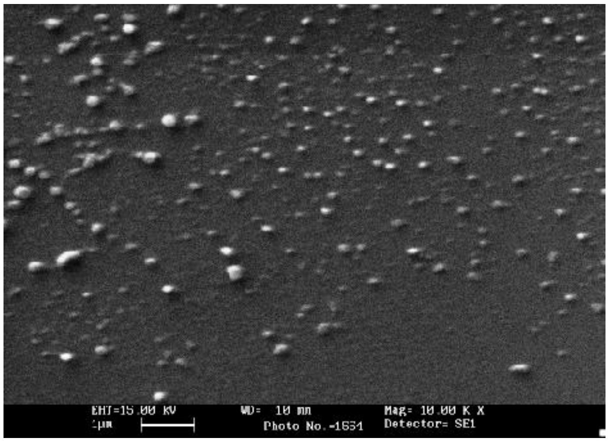
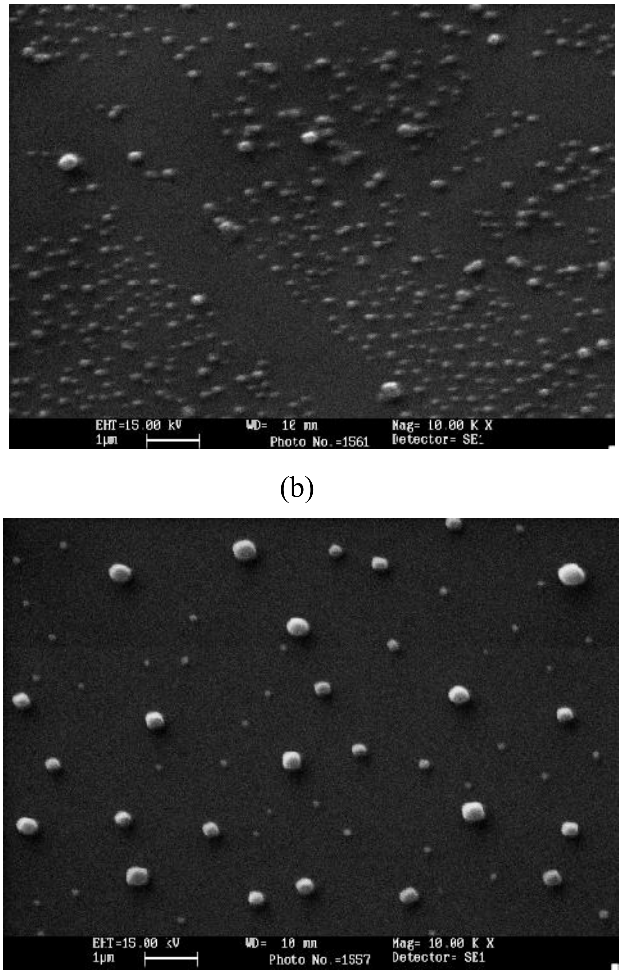


Fig.1: TEM image of WO_3 solution.

According to TEM results, the size of WO_3 nanoparticles are about 10-20 nm**.** In the interaction between gas and surface, the diffusion rate of gas into the layer depends on the diffusion coefficient as well as surface morphology. Therefore, the surface morphology should be studied first. For this purpose, the samples are doped with Pd in different annealing temperatures; then, their images are taken by SEM. The results obtained from 0.05M catalyst solution and with respecting to the SEM images, taken by Leo440i microscope at 20KV voltage, are summarized as follows:



(a)



(b)

(c)

Fig.2: SEM images of Pd-doped WO_3, annealed at a) 200˚C,b) 300˚C and c)400˚C.

The XRDs of the layers are studied in the range of $2\theta = 20°$ to $80°$. In order to determine, the structure of layers, the spectra are taken by STADI MP at 40 V and 30mA before and after doping the layers with Pd at different temperatures. Annealing the layer is resulted the rearrangement of atoms in it. The layer re-crystallization is started at 300˚C and completed at 500˚C. This fact is very effective in the layer characterization.

XRD spectra have been prepared at different temperatures before and after depositing $PdCl_2$ solution on the layers in order to determine the peaks of WO_3 and Pd, and shown in Figures 3 to 6.

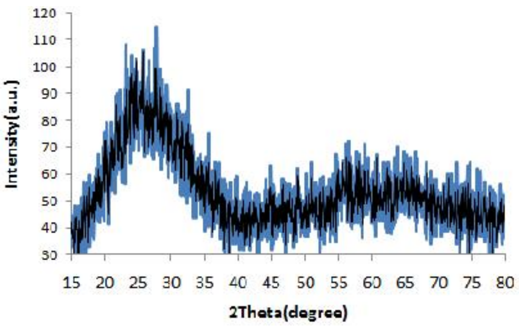
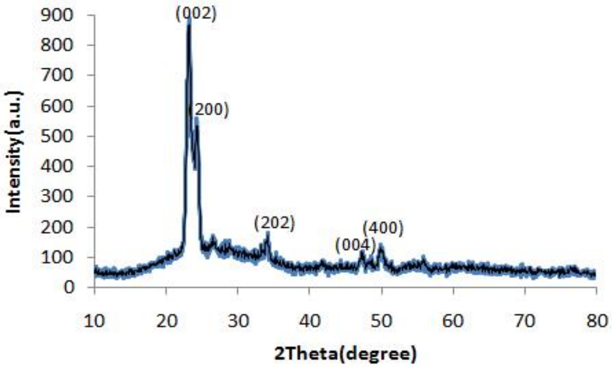
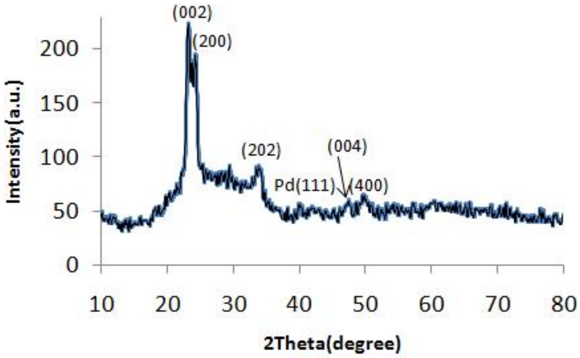


Fig.3: XRD spectra of un-doped WO_3 thin film, annealed at 200°C.

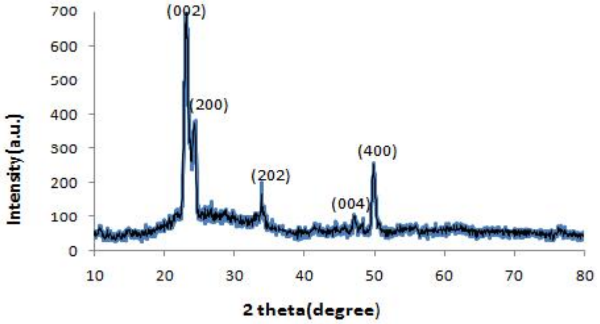


(a)

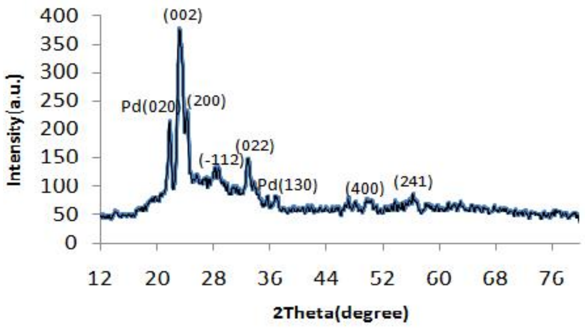


(b)

Fig.4: XRD spectra of WO_3 thin film a) un-doped b) Pd-doped (0.05M), annealed at 300°C.



(a)



(b)

Fig.5: XRD spectra of WO_3 thin film a) un-doped b) Pd-doped (0.05M), annealed at 400˚C.

According to Figure 3, the thin films of WO_3, annealed at 200˚C, are totally amorphous as no refractive peak is observed in the figure. Only one broad peak is seen in the range of 20˚ to 40˚, showing very little ordering and large extend of amorphous shape within the layers.

Figure 4 shows the XRD image of the sample annealed at 300˚C. The presence of a few refractive peaks indicates that increasing the temperature is resulted in improving the crystalline structure of WO_3 layers. Of course the structure is still amorphous with no perfect crystalline order. In this sample 5 peaks are observed at $2\theta = 23.16^\circ, 24.28^\circ, 34.12^\circ, 47.24^\circ$ and 49.92° that represent the crystalline directions of (002), (200), (202), (004) and (400), respectively. Therefore, the crystallized parts of sample, annealed at 300˚C, have triclinic symmetry.

Figure 5 shows more crystalline peaks in a larger extend in comparison with the sample, annealed at 300˚C. According to the figure, increasing the annealing temperature is ended in crystallizing of WO_3 layers. These samples, annealed at 400˚C, represent 5 main peaks at $2\theta = 23.12^\circ, 24.36^\circ, 33.84^\circ, 47.08^\circ$ and 49.88° indicating the crystalline directions of (002),(200),(202),(004) and (400), respectively. Therefore, the crystallized parts of the sample, annealed at 400˚C have monoclinic symmetry.

The WO_3 peaks increase with increasing the temperatures. They are observed almost in any directions at 500˚C indicating the complete crystallization of the sample. The XRD spectra of Pd-doped WO3 layers, annealed at 500˚C, are presented in Figure 6.

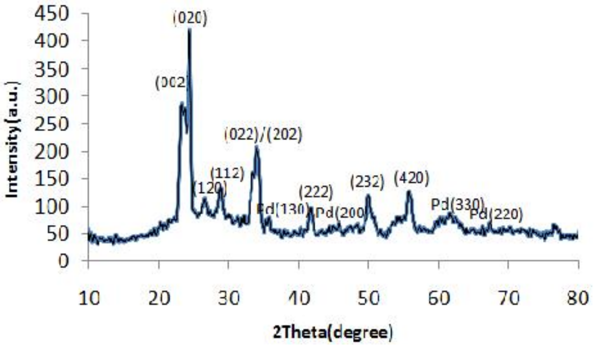


Fig.6: XRD spectra of Pd-doped WO_3 thin film (0.05M),annealed at 500˚C.

Indeed the spectra of un-doped WO_3 and Pd-doped WO_3 show that both monoclinic crystalline structures with discoid crystalline growth are in the same directions. The crystal structures have lost completely their water at 500˚C.

The amorphous layers are used for gasochromic devices, formed by tungsten trioxide. The increasing in the temperature and consequently more crystallization of layers is resulted in the increasing of sizes and core coherence of the particles. Therefore, the entrance and exit of ions and electrons from the layers are taken place more difficultly and in longer time. This fact is resulted in decreasing the transparency variation and reducing the reverse reactions of the layers.

The optical properties of the samples have been investigated by spectrophotometer. Their optical transmission graphs have been plotted versus wavelength before and after exposing to 2.7% hydrogen gas, applying 10litr/min oxygen for 1 minute. UV-visible spectrophotometer (Ocean Optics) has been used for this purpose. Figure 7 shows the transmittance spectrum of Pd-doped WO_3 thin film in optimum temperature.

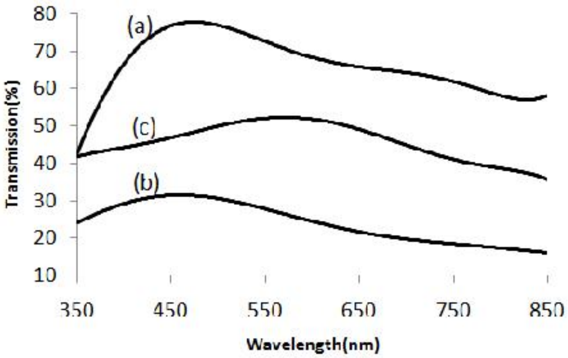


Fig.7: transmission spectrum versus wavelength at 300˚C annealing temperature a) before and b) after exposure to hydrogen, respectively and c) after applying oxygen gas flow for 1 min.)

The ΔT data of Pd-doped WO_3 thin films at 450nm wavelength are presented in Table.1 at different temperatures and after flushing 2.7% H_2 and 10 litr/min O_2 for 1minute.

Table 1. transmission modulation for Pd-doped WO3 layers at 450nm and different temperature

Film specification	ΔT % at 200˚C	ΔT % at 300˚C	ΔT % at 400˚C	ΔT % at 500˚C
After 2.7% H_2 (a-b)	13%	47%	30%	22%
After 10 lit/min O_2 (c-b)	5%	22%	3%	1%

Based on this table, maximum transparency variation is observed at 300˚C, after applying hydrogen and oxygen gases. To explain poor transmittance changes at the temperatures below 300˚C, it can be said that, the reactants do not receive enough activation energy (E_a) at low annealing temperatures for performing the reactions. In such a situation, WO_{3-x} cannot be converted to WO_3. Therefore, after applying hydrogen, a few number of WO_3 lattices (grains), are converted to WO_2 resulting in lower color changes.

On the other hand, at the temperatures over 300˚C, the samples are gradually more crystallized up to 400˚C and higher, converting to almost complete crystalline lattice. This increasing in crystallization at higher temperatures means more regularity in gasochromic material. This ordination is a barrier in transforming the crystal lattice to WO_2 after applying hydrogen gas. Consequently, the ΔTs of samples are reduced comparing to those at 300˚C.

The recorded response times of samples are 2, 3, 5 and 7sec., at 200, 300, 400 and 500˚C, respectively. According to these results, the samples respond to hydrogen later at higher temperatures. It means that at higher temperatures, structure changing is more difficult and takes longer time because of increasing the crystallization level.

On the other hand, after exposing to oxygen, the samples, annealed at higher temperatures, respond to oxygen later and return to their transparency later than amorphous templates. As it is seen in Table1, the samples, baked at 400 and 500˚C, return slightly to their initial transparencies. No significant returning is seen in the samples, annealed at 500˚C.

Long reverse times of crystalline samples are due to the order of atoms. This order acts as a barrier for conversion after exposing to oxygen. Therefore, the transparency of these samples change more difficultly and more lately.

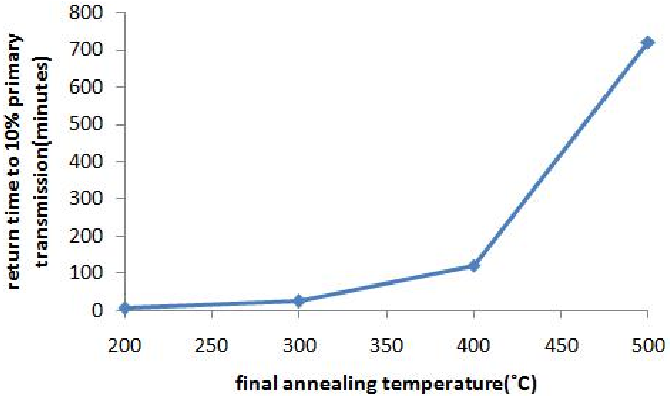


Fig.8: Reverse time of samples with different annealing temperatures in the air.

The samples are also tested at 300˚C with different concentration of $PdCl_2$ solution (0.01M, 0.05M and 0.1M). Other conditions are considered as previous. The graphs of spectrophotometer of samples with different $PdCl_2$ solution are plotted and ΔT data of the Pd-doped WO_3 thin films at 450nm wavelength is shown in Figures 9 and 10.

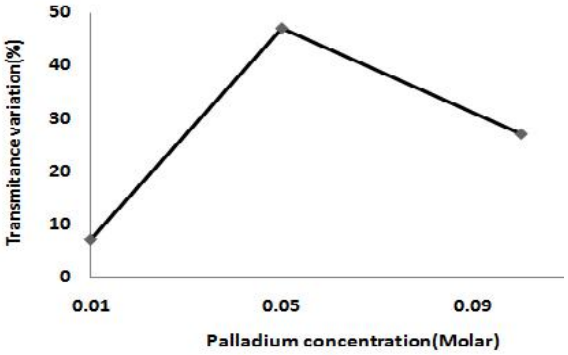


Fig.9: graph of transmittance variation versus catalyst concentration (a-b) with 0.01M, 0.05M and 0.1M of Pd catalyst after applying 2.7% hydrogen. (Annealing temperature was 300˚C)

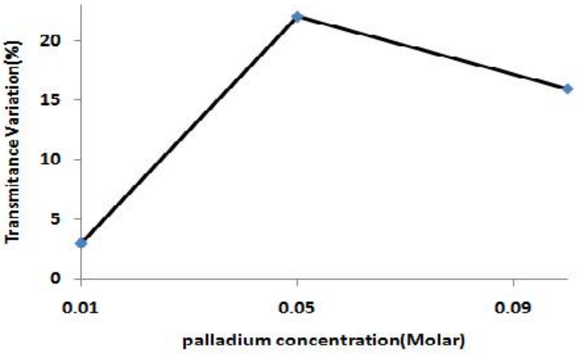


Fig.10: graph of transmittance variation versus catalyst concentration in returning to initial transmission(c-b) with 0.01M, 0.05M and 0.1M of Pd catalyst after applying 1 minute oxygen. (Annealing temperature was 300˚C)

Table2. transmission modulation for Pd-doped WO3 layers annealed at 300˚C, measured at 450nm, at different concentration of Pd catalyst.

Film specification	ΔT % at 0.01M	ΔT % at 0.05M	ΔT % at 0.1M
After 2.7% H_2 (a-b)	14%	47%	30%
After 10 litr/min O_2 (c-b)	3%	22%	17%

Table 2 shows that the optimum concentration of catalyst solution in gasochromic device is 0.05M.

4. Conclusion:

In this study, nano structure of WO_3 as well as catalyst solution has been prepared by sol-gel method. Several thin films of both WO_3 and Pd solution have been coated on the glass by spin coating technique. The size of WO_3 (10-20nm) is measured using TEM images. XRD patterns of the samples indicate that the WO_3 thin films, annealed at 200˚C, are amorphous. Moreover increasing in the annealing temperature is resulted in crystallization of tungsten oxide layers in such a way that it is completely crystallized at 500˚C and loses its water. The thin films, annealed at 300˚C and coated by 0.05M catalyst solution, show the most appropriate gasochromic properties. Accordingly and based on the results, the transmission spectra of WO_3 films with the mentioned condition have highest transparency changes and best coloration. They show proper response time and recovery time as well.

At the temperatures lower than 300˚C, WO_{3-x} cannot be converted to WO_3, because of not enough activation energy. Therefore, after applying hydrogen, a few number of WO_3 lattice, are converted to WO_2 resulting in lower color changes.

On the other hand, at the temperatures higher than 300˚C, the increasing in lattice crystallization is resulted in regularity increment which acts as a barrier in transformation of crystal lattice to WO_2 after applying hydrogen gas. Therefore, the ΔT of samples is reduced comparing to those at 300˚C. This regularity is also the main reason for increasing the recovery time.

In the optimal condition, ΔT gained as 47% after exposing to 2.7% hydrogen gas and as 22%, after flushed with 10 litr/min of oxygen gas for 1 minute. The values of response time and reverse time, obtained in this study, are 3sec. and 25sec., respectively.

References

[1]. Chih-Chieh Chan, Wen-Chia Hsu, Chung-Chieh Chang, Chao-Sheng Hsu, Hydrogen incorporation in gasochromic coloration of sol–gel WO3 thin films, Sensors and Actuators B 157 2011; 504–509.

[2]. A. Georg, W. Graf, D. Schweiger, V. Wittwer, P. Nitz, H.R. Wilson, Switchable glazing with a large dynamic range in total solar energy transmittance (TSET), Sol. Energy 62 .1998; 215–228.

[3]. V. Wittwer, M. Datz, J. Ell, A. Georg, W. Graf, G. Walze, Gasochromic windows, Sol. Energy Mater. Sol. Cells 84. 2004; 305–314.

[4]. C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Ams- terdam, 2002; p. 197.

[5]. V. Vitry, F. Renaux, R. Gouttebaron, J.P. Dauchot, M. Hecq, Thin Solid Films 502. 2006; 265.

[6]. R. Ghosh , M.B. Baker, R. Lopez , Optical properties and aging of gasochromic WO3, Thin Solid Films 518. 2010; 2247–2249.

[7]. M. Stolze, D. Gogova, L.-K. Thomas, Thin Solid Films 476. 2005;185–189.

[8] C.O. Avellaneda, L.O.S. Bulho˜ esi, Solid State Ionics 165 (2003) 117–121. [10] J.R. Tesmer, M. Nastasi (Eds.), Handbook of Modern Ion Beam Materials Analysis, Materials Research Society, Pittsburgh, 1995; pp. 83–138.

[9]. L. Zhuang, X. Xu, H. Shen, A study on the gasochromic properties of WO3 thin films, Surf. Coat. Technol. 167 .2003; 217–220.

[10] M. Zayat, R. Reisfeld, H. Minti, B. Orel, F. Svegl, Gasochromic effect in platinum- doped tungsten trioxide films prepared by the sol–gel method, J. Sol–Gel Sci. Technol. 11. 1998; 161–168.

[11]. B. Orel, N. Groselj, U. Opara Krasovec, M. Gabrscek, P. Bukovec, R. Reisfeld,,Gasochromic effect of palladium doped peroxopolytungstic acid films prepared by the sol–gel route, Sens. Actuators B 50.1998; 234–245.

[12]. Christian Salinga, Hansjo¨ rg Weis, Matthias Wuttig, Gasochromic switching of tungsten oxide films: a correlation between film properties and coloration kinetics, Thin Solid Films 414. 2002; 275–282.

[13]. A. Georg, W. Graf, R. Neumann, V. Wittwer, Thin Solid Films 384. 2001;269–275.

[14]. M. Ranjbar , N. Tahmasebi Garavand, S.M. Mahdavi, A. Iraji zad , Electroless plating of palladium on WO3 films for gasochromic applications, Solar Energy Materials & Solar Cells 94. 2010; 201–206.

[15]. Lin Zhuanga, Xueqing Xub, Hui Shen, A study on the gasochromic properties of WO3, Surface and Coatings Technology 167. 2003; 217–220.

[16]. Kudo T., Okamoto H., Matsumoto K. and Sasaki Y.,"Peroxopolytungstic acids synthesized by direct reaction of tungsten or tungsten carbide with hydrogen peroxide",Inorganica Chim Acta, 1986;vol. 111.