

# Study of Gasochromic Pt-decorated WO<sub>3</sub> thin films synthesized via the Sol-Gel Route

Dr. Nisha<sup>1</sup>, Megha Narayan<sup>1\*</sup>, Dr. Palash Kumar Basu<sup>2</sup>

<sup>1</sup>Assistant Professor, Sahyadri College of Engineering and Management,  
Email:nishashreyan@gmail.com;

<sup>2</sup>Professor, IIST, Thrivandrum, Email: palasbasu.sensor@gmail.com

\*megha.cc@sahyadri.edu.in

**Abstract.** Metal Oxide-based Chemi-resistive sensors for hydrogen gas detection utilize microheaters, posing a risk of explosion due to electric sparks, as hydrogen concentrations above 4% are highly flammable. Gasochromic sensors, on the other hand, are safe as they can detect target gases based on changes in optical transmittance at room temperature. The transmittance of synthesized films changes reversibly when the target gas is alternatively purged and stopped. In the proposed work, noble metal-doped WO<sub>3</sub> thin films are synthesized via the sol-gel route followed by spin coating. UV-VIS-NIR transmittance spectra for the samples were measured at room temperature by alternatively exposing the samples to 4% Hydrogen and synthetic air. The results show that gasochromic sensing can be enhanced by increasing the doping concentration to 2wt%. The better sensing could be linked to the fine dispersal of the Pt nanoparticles on WO<sub>3</sub> thin films, facilitating the adsorption and hydrogenation of molecular hydrogen.

## 1 Introduction

Hydrogen gas is a highly sought-after sustainable source of renewable energy that has the potential to supersede fossil fuels in the future. It is a colorless, odorless gas with low ignition energy that can easily seep through minor breaches due to its small atomic size. Identifying hydrogen leaks at storage facilities and during transportation is essential because hydrogen, combined with ambient oxygen, is highly flammable. The traditional approach to gas detection has drawbacks like high cost, limited miniaturization, complex equipment requiring direct intervention, selectivity towards a particular gas, and is unsuitable for low concentration detection. In recent decades, metal oxide-based chemiresistive gas sensors have become a popular approach for monitoring dangerous and flammable gases [1], [2]. They exhibit higher sensitivity and response and are suitable for low-concentration gas detection. However, humidity and other external factors will affect their performance in the long run. They are susceptible to cross-sensitivity to other gases and electromagnetic interference and operate at high temperatures.

Tungsten oxide (WO<sub>3</sub>) is a transition metal oxide semiconductor of n-type having a broad band gap and distinct electrical and optical properties [3]. It has chromic qualities that allow the optical transmittance to change from transparent to colored states when exposed to external potential, Ultra Violet (UV) radiation, thermal energy, and hydrogen gas [4].

Gasochromism refers to reversible shifts in the optical transmittance when the sensing layer comes in contact with Hydrogen gas [5][6].  $\text{WO}_3$  thin films are transparent in the Ultraviolet-Visible (UV-VIS) range; upon exposure to hydrogen gas, they turn deep blue in color, and transmittance drops. Exposure to ambient air or oxygen can achieve the initial transmittance. Gasochromic film can be prepared by sputtering a thin deposition of a noble metal such as Platinum (Pt), Palladium (Pd), or Gold (Au) over  $\text{WO}_3$  or by introducing nanoparticles of the dopants into its crystal lattice.

Several studies have been reported on the gasochromic detection of Pt/ $\text{WO}_3$  or Pd/ $\text{WO}_3$  thin films over the past years. Se-Hee Lee et al. [7] reported gasochromic phenomenon in Pd/a- $\text{WO}_3$  thin films with a focus on Raman scattering. Wen Chia Hsu et al. [8] synthesized gasochromic films by the electrodeposition method, followed by sputtering of the Pt layer. In spite of the films demonstrating higher response and recovery times, the transmittance change ( $\Delta T$ ) observed at 5 mol% was 2%.

Nanostructured dopant particles possess a large surface area, which provides an adequate count of active sites for hydrogen adsorption and subsequent redox reactions. They reduce the activation energy required for hydrogen reactions on  $\text{WO}_3$  [9].

In this investigation,  $\text{WO}_3$  films were grown by the sol-gel method from Peroxo Tungstic Acid (PTA) solutions, then spin-coated over glass substrates. The concentration of Pt dopant was varied between 0.5 and 2 wt%. For each of these samples, the Ultra Visible – Near Infrared (UV-VIS-NIR) optical transmittance changes were captured by alternatively subjecting the prepared films to 4% hydrogen gas (in nitrogen balance) and Synthetic Air (SA, 80%  $\text{N}_2$ +20%  $\text{O}_2$ ). On the optimized sample, material characterization was performed to examine the impact of structural alteration brought on by dopants on the gasochromic hydrogen sensing performance.

## 2 Materials and Preparation

### 2.1 Substances and Reagent

Sodium tungstate dihydrate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\geq 99\%$ ), Hydrogen peroxide (30wt%), and Nitric Acid ( $\text{HNO}_3$ , 68%, Merck) utilized in this work were bought from Sigma-Aldrich. Reagents and chemicals used were of lab grade, acquired, and consumed without being cleaned further. Transparent glass substrates served as the base substrate. Before usage, they were rinsed in Iso Propyl Alcohol followed by Deionised water (DI water) in an ultrasonicator.

### 2.2 Sol-Gel Synthesis of Pt/ $\text{WO}_3$ Thin Films

The synthesis method involves dissolving sodium tungstate dihydrate salt in hydrogen peroxide to form Peroxy Tungstic Acid (PTA), which is rich in  $\text{W}_2\text{O}_{11}^{2-}$  species and is stable at room temperature [10]. 0.03M of the precursor solution was prepared by dissolving  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  salt in 100ml of DI water. Concentrated  $\text{HNO}_3$  is then added dropwise until the pale yellow-colored gel is formed. This gel has a short life, which transforms into yellow colored tungstic acid powder. In order to prevent this,  $\text{H}_2\text{O}_2$  is introduced gradually under stirring till a clear transparent solution is obtained. Ethanol is used as a stabilizing agent, and the solution is mixed with 30ml. This solution is then kept for three days of aging.

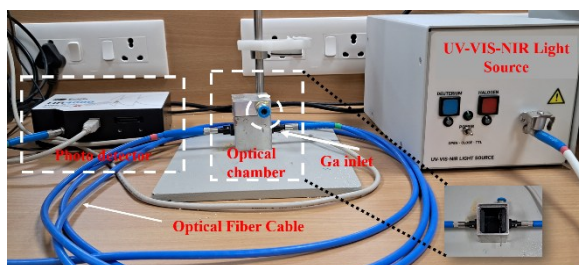
To synthesize Pt nanoparticles, 0.1M Hexachloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) is mixed in 10 ml of DI water. Next, 2 ml of concentrated HCl is introduced under constant stirring for 8 hours. The Pt/ $\text{WO}_3$  samples were then prepared by adding the Pt solution to the

WO<sub>3</sub> sol to get concentrations, as mentioned in Table 1. The sol is deposited on a clean glass substrate by spin-coating at a rate of 1000 rpm, and air annealed at 300°C for 1 hour.

**Table 1.** List of the prepared samples and their doping concentration

Sample	Pt doping concentration (Wt%)
WO <sub>3</sub> -0.5Pt	0.5
WO <sub>3</sub> -1Pt	1
WO <sub>3</sub> -2Pt	2
WO <sub>3</sub> -3Pt	3

### 2.3 Experimental Setup for Optical H<sub>2</sub> sensing



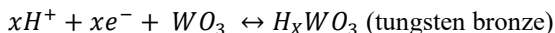
**Fig. 1a.** Experimental setup for gasochromic Hydrogen Sensing

Figure 1a. shows the experimental setup to investigate the gasochromic H<sub>2</sub> sensing properties of the Pt/WO<sub>3</sub> samples. The apparatus consists of a customized gas chamber with provisions for connecting optical fiber cables, through which it is linked to a UV-VIS-NIR light source (wavelength range 190-2500nm) and a photodetector. Additionally has an inlet and outlet for a gas connection. The internal structure of the optical chamber has clamps to hold the gasochromic film. The photodetector is connected to a PC through a USB cable. The UV-VIS-NIR transmittance changes of the samples are recorded by alternatively purging the chamber with 4% H<sub>2</sub> gas in N<sub>2</sub> balance and synthetic air in the wavelength range of 300-1000nm. When gasochromic films are exposed to hydrogen gas, their transmittance decreases; however, initial transparency can be restored by purging with either oxygen or air.

## 3 Results and Discussion

### 3.1 Gasochromic Mechanism

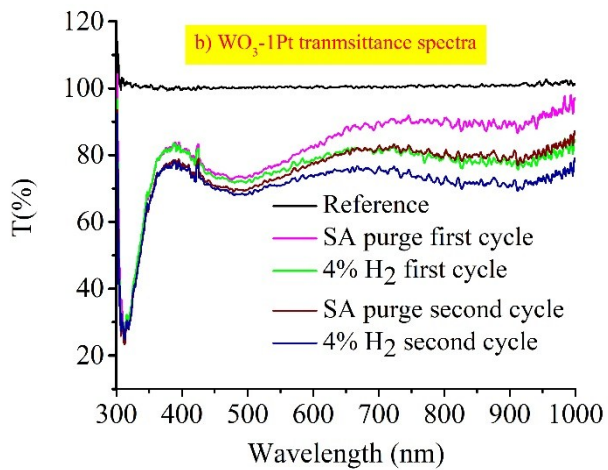
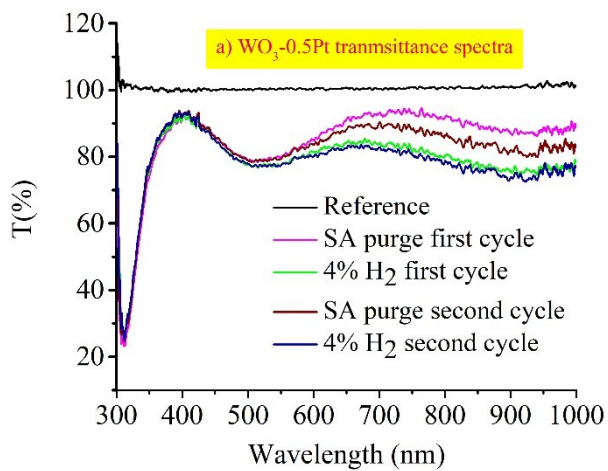
The gasochromic effect in Pt or Pd-doped  $WO_3$  films is caused by the injection of  $H^+$  ions along with electrons, resulting in the formation of tungsten bronze as given by the equation [11][6],

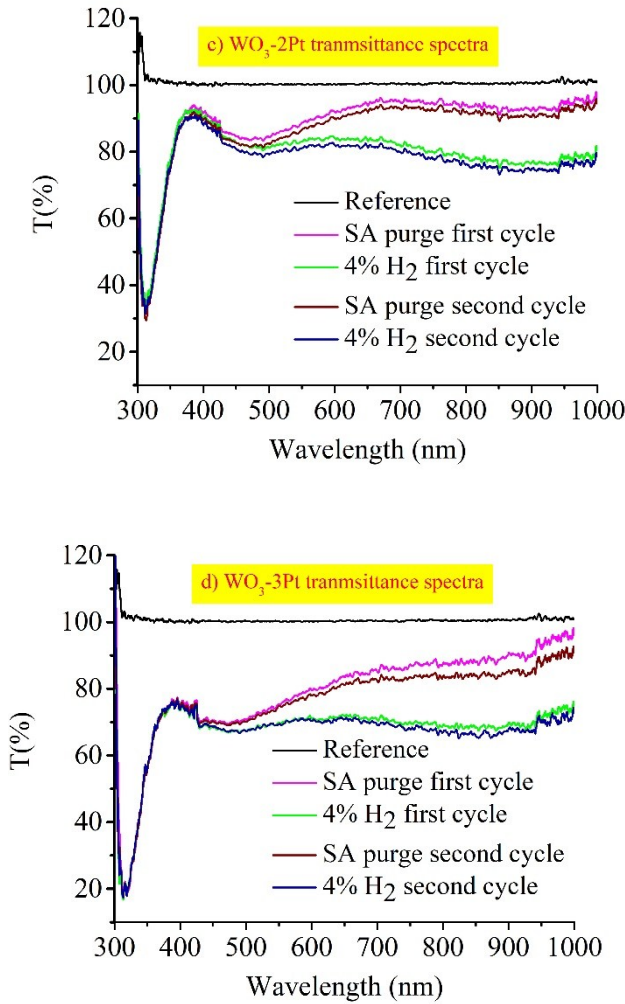


Pt is known for its excellent hydrogenation properties [12]. By chemical sensitization of  $WO_3$  with Pt nanoparticles, it is possible to improve the gas sensing and selectivity towards hydrogen [9]. By the catalytic action of Pt, the molecular Hydrogen ( $H_2$ ) is split into Hydrogen atoms and permeates into the  $WO_3$  layer as  $H^+$  ions and electrons forming tungsten bronze[5], [6]. In stoichiometric  $WO_3$ , tungsten is in the  $6^+$  oxidation state ( $W^{6+}$ ). Intercalation of cations and electrons results in redox reactions, reducing the tungsten oxidation state to  $5^+$  ( $W^{5+}$ ). Tungsten bronze gives a deep blue color to the film, which has low transmittance.

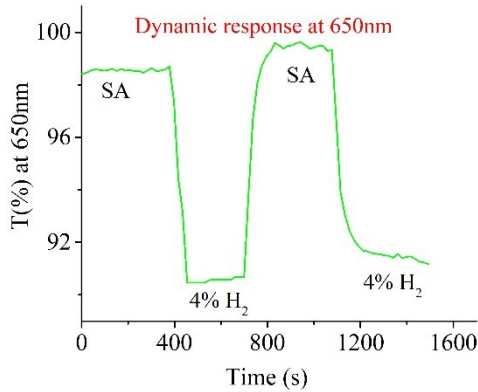
### 3.2 Optical $H_2$ Sensing

Optical transmittance changes are recorded for the prepared samples by alternatively exposing them to 4%  $H_2$  in  $N_2$  balance and SA for 10 minutes each. All the measurements were done at Room Temperature (RT). Figure 2 (a-d) reveals the transmittance plots of the samples at RT. It became apparent that the transmittance changes are wavelength-influenced, with a maximum in the visible-NIR spectrum. The transmittance of the samples drops when purged with hydrogen gas and tends to increase when exposed to SA. The transmittance change  $\Delta T = T - T_0$  is the variation between the gasochromic film's transmittance when it is coloured and bleached. The gasochromic performance is easily examined by calculating the optical density change ( $\Delta OD$ ). This quantifies the colour centres created when  $W^{6+}$  is reduced to  $W^{5+}$ , given by  $\Delta OD = \log (T_0/T)_\lambda$ , where  $T_0$  – original transmittance (state of bleaching),  $T$ - final transmittance (colored state), measurements are performed at a specific wavelength ( $\lambda$ ). Transmittance dynamics are examined at a single wavelength of  $\lambda=650$  nm to eliminate any heating effect at higher wavelengths. Samples  $WO_3$ -2Pt and  $WO_3$ -3Pt exhibited more significant  $\Delta T$  of 22 and 21, respectively, at 650nm. On the other hand, samples with low doping concentrations had lower  $\Delta T$  values (figure 2(a-b)). This could be due to the very few active sites available for gas reactions in these samples due to their low dopant concentrations. With repeated cycles of alternate hydrogen and SA purge, it was observed that recovery to initial transmittance was poor for the samples  $WO_3$ -0.5Pt and  $WO_3$ -1Pt. For sample  $WO_3$ -2Pt (**figure 2c**), the difference in the transmittance between the first and second gas purge cycles was less than 2%. This was maintained with multiple cycles of  $H_2$  and SA purge, indicating its good recovery compared to other samples. Whereas for sample  $WO_3$ -3Pt (**figure 2d**), this change was not constant, with several cycles involving a gas purge.



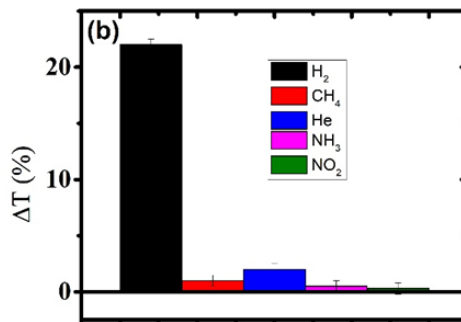


**Fig. 2.** Optical transmittance spectra of the sample a) WO<sub>3</sub>-0.5Pt b) WO<sub>3</sub>-1Pt c) WO<sub>3</sub>-2Pt d) WO<sub>3</sub>-3Pt measured at room temperature for 4% H<sub>2</sub> in N<sub>2</sub> balance.

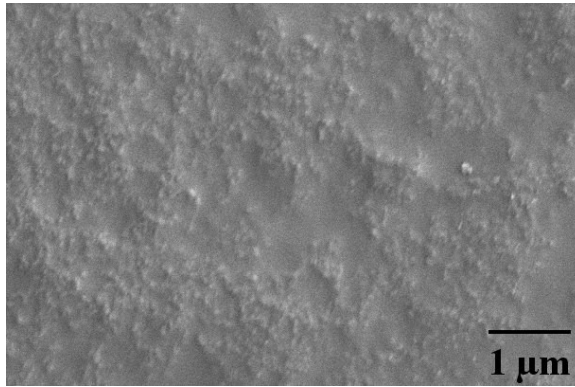


**Fig. 2e.** Dynamic transmittance response of WO<sub>3</sub>-2Pt at 650nm for 4% H<sub>2</sub> in N<sub>2</sub> balance

For sample WO<sub>3</sub>-2Pt giving optimum gasochromic response, the dynamic transmittance was recorded at 650nm wavelength as shown in **figure 2e**. Even at RT, the sample had a good response and recovery times within 40 s. One of the common issues faced by hydrogen sensors is the cross sensitivity to Helium (He) gas especially chemiresistive sensors. However the proposed gasochromic samples were highly selective towards Hydrogen and the response didn't change in the presence of Helium gas. **Figure 2f** shows the cross cross-sensitivity of the gasochromic films have been recorded for gases including 4% He, CH<sub>4</sub>, NH<sub>3</sub>, and NO<sub>2</sub>. The Scanning Electron Microscope (SEM) image of the prepared sample is given in **figure 2g**. The surface was rough with irregular bumps formed by aggregation of WO<sub>3</sub> nanoparticles of average size 30nm. The surface was crack-free, indicating a uniform deposition. Because of their extreme dispersion, Pt nanoparticles were not discernible in the SEM image, which is typically observed in sol-gel deposited samples. The experiment has repeated with a year old sample and the response was still good with change less than 0.2% when did with a newly prepared sample indicating the better stability of the prepared samples. Table 2 gives a comparison of the transmittance changes, response and recovery times of previous Pt and Pd doped gasochromic sensors with the reported work.



**Fig. 2f.** Cross sensitivity towards different gases.



**Fig. 2g.** SEM image of WO<sub>3</sub>-2Pt

**Table 2.** Comparison of the previous gasochromic sensors with proposed work.

Gasochromic Material	$\Delta T$ (%) or $\Delta OD$	Response / Recovery time (s)	Reference No.
H <sub>2</sub> reduction of drop dried PdCl <sub>2</sub> /PLD WO <sub>3</sub>	Amorphous films showed higher $\Delta OD$ below 100°C and polycrystalline films in the operating temp. 90-100°C	Faster response around 100-110°C	[13]
Sol-gel Pt/WO <sub>3</sub>	60% in RT	10s/150s in RT	[14]
Sol-gel Pd/WO <sub>3</sub>	~50% in RT	~60s	[9]
Sputtered Pt/Electrode sited WO <sub>3</sub>	~2% for 5% H <sub>2</sub> and 22% for 50% H <sub>2</sub> at RT at 770 nm	5s/60s	[14]
Sol-gel Pt/WO <sub>3</sub>	~10% at RT	~ 40s/40s	This work

## 4 Conclusion

Nanostructured Pt/WO<sub>3</sub> thin films were prepared using the inexpensive sol-gel spin coating method. As deposited samples were uniform, as observed from the SEM image with high dispersion of Pt nanoparticles. As seen in the case of WO<sub>3</sub>-2Pt, increasing Pt doping has aided the samples' gasochromic responses with better response and recovery. They are potential applications for hydrogen safety sensors due to their electrical-free room temperature operation.

## References

- [1] A. Dey, "Semiconductor metal oxide gas sensors: A review," *Mater. Sci. Eng. B*, vol. 229, pp. 206–217, 2018.
- [2] M. A. Carpenter, S. Mathur, and A. Kolmakov, *Metal oxide nanomaterials for chemical sensors*. Springer Science & Business Media, 2012.
- [3] M. Ranjbar, A. Irajizad, and S. M. Mahdavi, "Gasochromic tungsten oxide thin films for optical hydrogen sensors," *J. Phys. D. Appl. Phys.*, vol. 41, no. 5, p. 55405, 2008, doi:10.1088/0022-3727/41/5/055405.
- [4] J.-H. Cho *et al.*, "Thermochromic characteristics of WO<sub>3</sub>-doped vanadium dioxide thin films prepared by sol-gel method," *Ceram. Int.*, vol. 38, pp. S589–S593, 2012, doi: <https://doi.org/10.1016/j.ceramint.2011.05.104>.
- [5] S.-H. Lee *et al.*, "Gasochromic mechanism in a-WO<sub>3</sub> thin films based on Raman spectroscopic studies," *J. Appl. Phys.*, vol. 88, no. 5, pp. 3076–3078, 2000.
- [6] C.-C. Chan, W.-C. Hsu, C.-C. Chang, and C.-S. Hsu, "Hydrogen incorporation in gasochromic coloration of sol-gel WO<sub>3</sub> thin films," *Sensors Actuators B Chem.*, vol. 157, no. 2, pp. 504–509, 2011, doi: <https://doi.org/10.1016/j.snb.2011.05.008>.
- [7] S. H. Lee *et al.*, "Gasochromic mechanism in [formula omitted] thin films based on Raman spectroscopic studies," *J. Appl. Phys.*, vol. 88, no. 5, pp. 3076–3078, 2000, doi: 10.1063/1.1287407.
- [8] W.-C. Hsu, C.-C. Chan, C.-H. Peng, and C.-C. Chang, "Hydrogen sensing characteristics of an electrodeposited WO<sub>3</sub> thin film gasochromic sensor activated by Pt catalyst," *Thin Solid Films*, vol. 516, no. 2, pp. 407–411, 2007, doi: <https://doi.org/10.1016/j.tsf.2007.07.055>.
- [9] S. Fardindoost, A. Irajizad, F. Rahimi, and R. Ghasempour, "Pd doped WO<sub>3</sub> films prepared by sol-gel process for hydrogen sensing," *Int. J. Hydrogen Energy*, vol. 35, no. 2, pp. 854–860, 2010, doi: <https://doi.org/10.1016/j.ijhydene.2009.11.033>.
- [10] N. Naseri, S. Yousefzadeh, E. Daryaei, and A. Z. Moshfegh, "Photoresponse and H<sub>2</sub> production of topographically controlled PEG assisted Sol-gel WO<sub>3</sub> nanocrystalline thin films," *Int. J. Hydrogen Energy*, vol. 36, no. 21, pp. 13461–13472, 2011, doi: <https://doi.org/10.1016/j.ijhydene.2011.07.129>.
- [11] C. G. Granqvist, "Electrochromic tungsten oxide films: Review of progress 1993–1998," *Sol. Energy Mater. Sol. Cells*, vol. 60, no. 3, pp. 201–262, Jan. 2000, doi: 10.1016/S0927-0248(99)00088-4.
- [12] A. Esfandiari, S. Ghasemi, A. Irajizad, O. Akhavan, and M. R. Gholami, "The decoration of TiO<sub>2</sub>/reduced graphene oxide by Pd and Pt nanoparticles for hydrogen gas sensing," *Int. J. Hydrogen Energy*, vol. 37, no. 20, pp. 15423–15432, 2012.
- [13] N. T. Garavand, S. M. Mahdavi, A. I. zad, and M. Ranjbar, "The effect of operating temperature on gasochromic properties of amorphous and polycrystalline pulsed laser deposited WO<sub>3</sub> films," *Sensors Actuators B Chem.*, vol. 169, pp. 284–290, 2012, doi: <https://doi.org/10.1016/j.snb.2012.04.082>.
- [14] S. Okazaki and S. Johjima, "Temperature dependence and degradation of gasochromic response behavior in hydrogen sensing with Pt/WO<sub>3</sub> thin film," *Thin Solid Films*, vol. 558, pp. 411–415, 2014, doi: <https://doi.org/10.1016/j.tsf.2014.02.080>.