

Gas-chromism in ultrasonic spray pyrolyzed tungsten oxide thin films

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Abstract. A simple and inexpensive ultrasonic spray pyrolysis (USP) technique has been employed to deposit tungsten oxide (WO_3) thin films by spraying 2.0 mM aqueous ammonium metatungstate solution onto the amorphous glass substrates kept at 250°C. The films were further annealed at 400°C for 4 h in air. X-ray diffraction (XRD) technique was used to determine the crystallinity and to identify the WO_3 phases. It was found that the films were sub-stoichiometric, WO_{3-x} . To study gas-induced properties, a catalyzing layer of platinum (Pt) was sputtered onto it. The gas-induced electrical and optical properties of Pt/ WO_3 /glass samples were studied and results reported. It was found that electrical resistivity decreased by a factor of 10 within 2 min and stabilized after 15 min, after H_2 gas exposure. Similarly the optical transmittance of the samples attenuated from 55% to 10% within 15–20 min. The reversible changes in electrical resistivity and optical transmittance were observed when the samples were exposed to oxygen. The response times and sensitivity of the samples were estimated.

Keywords. Ultrasonic spray pyrolysis; tungsten oxide; thin films; gas-chromism.

1. Introduction

Optically active thin film coatings can alter their optical properties as a function of changes in external conditions. The changeable optical characteristics can be obtained by different physical and chemical processes, in a large number of materials. These materials, recently named chromogenics (Lampert and Granqvist 1990), embrace both inorganic and organic materials. Optical coatings of these materials on architectural components are part of a programme aimed at reducing the cost of heating and cooling buildings. These materials flip between opaque and transparent states, when exposed to the gases and activated with a catalyzing layer they are known as 'gas-chromic'. They transmit sunlight nearly as well as a double-glazed window. They have no electrodes so they consist of only two layers and transmit more than 80% of all solar radiation. The suitability of the material to be used as gas-chromic depends on its ability to return to its initial state upon removal of the cause that induced the change of its properties. Up to now, many materials have shown gas-chromic effect. Among them are SnO_2 for the flammable gases (Kamimori *et al* 1994), palladium for hydrogen (Hofheins *et al* 1995), (Ti, Sn) O_2 for CO, C_3H_8 , $\text{C}_2\text{H}_5\text{OH}$ and H_2 gases (Arakawa *et al* 1999) and WO_3 for nitrogen oxides (Akiyama *et al* 1993) and H_2S (Dwyer 1991).

Generally, the gas-chromic systems are described as having the configuration: Catalyzing metal/insertion compound (semiconductor)/insulator. WO_3 is the most extensively studied insertion compound, which exhibits pronounced gas-chromism. The platinized bulk WO_3 reacts with H_2 at room temperature to form blue colour. This was first

recognized by Khoobar in 1964. After this, several other catalyzing materials viz. Pd (Hobbs and Tseung 1972), optically semitransparent Pt (Degani *et al* 1987), Rh (Porter *et al* 1985) and Au (Davazoglou and Georgouleas 1998) were studied in the gas-chromic devices based on WO_3 . The WO_3 films have been deposited mainly by using chemical vapour deposition and vacuum evaporation techniques.

The goal of this investigation was to examine the gas-chromic effect in USP- WO_3 thin films with Pt as a catalyzing material. The change in electrical resistivity and optical transmittance properties of Pt/ WO_3 tandem samples, in presence of hydrogen and oxygen gases were studied. The preliminary results are reported.

2. Experimental

Ultrasonic spray pyrolysis involves the application of a fine mist of very small droplets containing the reactants onto the hot substrates. The critical operations of the spray pyrolysis technique are the preparation of uniform and fine droplets and the controlled thermal decomposition of these droplets.

Figure 1 shows a schematic diagram of the USP system used in the present study. It consists of a quartz reactor, a r.f. heater, ultrasonic nozzle and an exhaust system. To prepare WO_3 thin films, the precursor solution was prepared by dissolving an appropriate quantity of hydrated ammonium metatungstate ($\text{H}_{26}\text{N}_6\text{O}_{41}\text{W}_{12}$) in doubly distilled water. The concentration of the solution was 2 mM. This solution was sprayed through the ultrasonic nozzle,

which was operated at 1 MHz, onto the preheated glass substrates. The substrate temperature was kept constant at 250°C and continuously monitored by a chromel-alumel thermocouple fixed to the metallic substrate holder. After many trials, the preparative parameters of the system were optimized to obtain uniform, pin hole free and adherent films of WO₃. These values are represented in table 1. After the deposition, the films were annealed at 400°C in air for 4 h.

The film thickness was measured using a Dektak 3030 profilometer. The structure of the films was examined by conventional XRD technique. The XRD measurements were performed in a θ -2 θ coupled geometry with a Siemens D-500 diffractometer using a copper anode.

After WO₃ films were annealed, a 10 nm thick layer of Pt was sputtered on to it. To obtain ohmic contacts for the electrical measurements, Au contacts were sputtered on Pt layer. The sample geometry is shown in figure 2. The samples were then placed in a glass chamber consisting of inlet and outlet for gases. At the beginning of the experiment, the chamber was filled with nitrogen. The samples were then exposed to a gas flow of 5 vol.% H₂ in 95 vol.% N₂ with 39 ml/min flow rate for about 30 min. After this, gas flow was terminated and 10 vol.% O₂ in 90 vol.% N₂ gas was allowed to flow inside the chamber with the same rate and time. The relative humidity and operating temperature were 10% and 23°C, respectively. The electrical resistivity was measured during H₂ and O₂ gas flows. The optical transmittance of the samples during the exposure of the gases was measured with the He-Ne laser ($\lambda = 633$ nm).

3. Results and discussion

During spray pyrolysis, the solution was atomized onto the preheated glass substrates. The droplets underwent

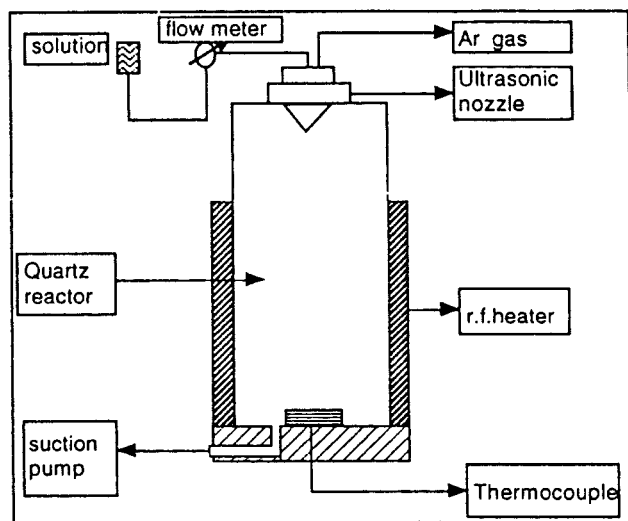
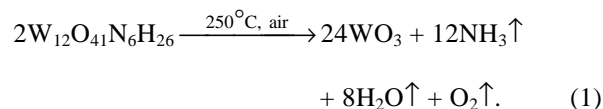


Figure 1. Schematic of USP technique for the deposition of WO₃ films.

evaporation, solute condensation and thermal decomposition which resulted in the film formation. In case of tungsten oxide thin films, following reaction took place:



The films were found to be uniform, pin hole free and well adherent to the amorphous glass substrates. The colour of the film was slightly whitish and changed to transparent yellow upon annealing at 400°C in air. Thickness of the film was 0.6 μm .

3.1 Structural determination of WO₃ thin films

Figure 3 shows XRD pattern of USP-WO₃ thin film annealed at 400°C in air for 4 h. It is observed that the films are polycrystalline and consist of well defined, high intense diffraction peaks corresponding to (020), (002), (220) and (400) planes. The 'd' values are compared with standard 'd' values from JCPDS data (35-270). The good agreement of 'd' values with this data indicates that the film structure is orthorhombic hydrated (0.33 H₂O) WO₃. Additionally, few peaks corresponding to (200), (-403), (504) (750) and (014) planes are observed, which are assigned to oxygen deficient tungsten oxide (JCPDS card Nos: 36-392 and 41-745). Therefore it is concluded that

Table 1. Various optimized preparative parameters for USP-WO₃ thin films.

Parameter	Optimized value
Nozzle to substrate distance	14 cm
Nozzle power	4.5 W
Nozzle frequency	1 MHz
Solution concentration	2 mM
Solution spray rate	1 ml/min
Quantity of solution sprayed	10 ml
Argon gas pressure	1 bar
Substrate temperature	250 \pm 2°C
Inner diameter of the quartz reactor	8.3 cm

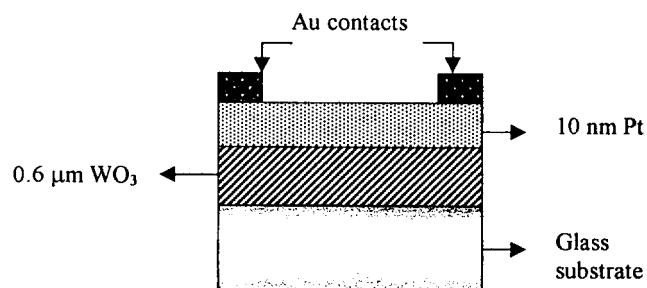


Figure 2. Various layers comprising gas-chromic sample.

the resultant USP-WO₃ films are sub-stoichiometric, WO_{3-z}. Analogous results are reported by others (Deneuville and Gerard 1978; Nanba and Yasui 1989).

3.2 Electrical resistivity measurements

Figure 4 shows the time evolution of the resistance of a Pt/WO₃ sample. It is observed that the resistance decreases significantly, by a factor of 10 in 2 min, in the presence of hydrogen. The response time (time interval necessary for the resistance to stabilize at its lowest value) is of the order of 14 to 16 min, while the recovery time (time interval necessary to return to its initial value) is ~ 24 min. The values of response times (response and recovery times) are found to be larger than the reported values (Shaver 1967; Davazoglou and Georgouleas 1998) for Pt/WO₃ and Au/WO₃ systems respectively. However the sensitivity of USP-WO₃ samples is found to be higher than the reported value (Davazoglou and Georgouleas 1998). This may be due to different structures of WO₃ films, which have resulted from various deposition techniques. Generally, the WO₃ films deposited by chemical deposition technique consisted of metallic W and WO₂ phases thereby exhibiting lower room temperature electrical resistivity (Davazoglou *et al* 1997). Whereas USP-WO₃ samples are hydrated and oxygen deficient phases, are more resistive than W or WO₂ (Rogers *et al* 1969). Additionally, the variable amount of hydration content in the films is responsible for these discrepancies.

The resistance drop in the presence of hydrogen is associated with the colouration while increase in resistance after the introduction of oxygen is associated with bleach-

ing process. Thus it is shown that coating based on USP-WO₃ turn blue in the presence of hydrogen and become transparent when exposed to oxygen.

The colouration and bleaching mechanism can be explained on the basis of a model proposed by Rye and Ricco (1987).

By an exposure of Pt/WO₃ with hydrogen, the dissociation of H₂ at the Pt surface is followed by a rapid diffusion of H to the Pt/WO₃ interface where a dipole layer is created. This results in a field across the interface, which in turn produces a sharp drop in the conduction band edge. This potential drop lowers the energy of the conduction band edge relative to the Fermi level of platinum and allows the charge transfer of electrons (hydrogen being electron donor) for the colouration of WO₃.

When oxygen is in contact with the sample interface, similar description can be used, as described for the hydrogen above. Oxygen in the gas phase induces bleaching, because oxygen diffuses in the film, removes an electron from coloured W⁵⁺ states, and can occupy the oxygen vacancy. Thereby sample attains its initial state.

3.3 Optical transmittance studies

Figure 5 shows transmittance versus time of the Pt/WO₃ sample during the exposure of H₂ and O₂ containing gases. The gas compositions and flow rates are same as used for electrical resistivity experiment. The incidence of light proceeds from the side where Pt is placed, as shown in the insert in figure 5. It is observed that, after H₂ gas is introduced transmittance (*T*) decreases rapidly and the saturation value is reached after about 15 min. While for O₂ gas, *T* increases relatively slowly and saturation is reached after 25 min. The transmittance changes between 10% to

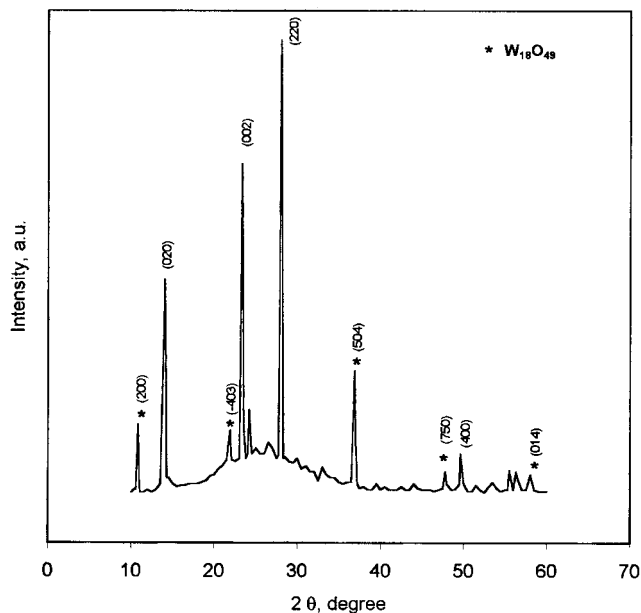


Figure 3. XRD pattern of USP-WO₃ film annealed at 400°C for 4 h.

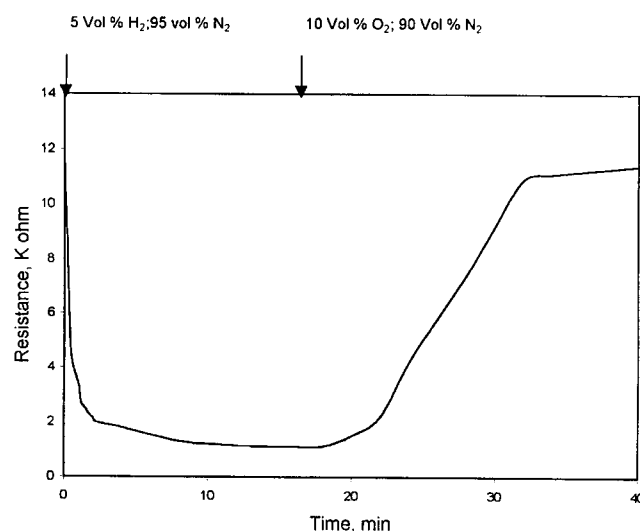


Figure 4. Variation of resistance with time for film Pt/WO₃ during exposure to 5 vol.% H₂ in 95 vol.% N₂ and 10 vol.% O₂ in 90 vol.% N₂.

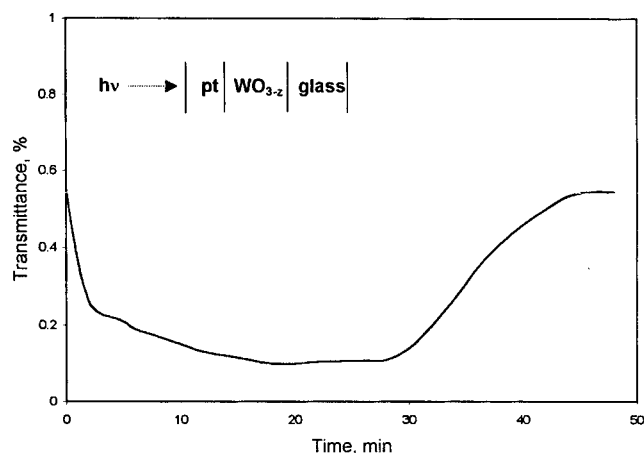


Figure 5. Variation of transmittance with time for Pt/WO₃ sample during exposure to 5 vol.% H₂ in 95 vol.% N₂ and 10 vol.% O₂ in 90 vol.% N₂.

55%. Above results suggest that colouration process in Pt/WO₃ is faster than the bleaching process.

Further it is anticipated that the response times, transmittance and sensitivity of Pt/WO₃ samples depend on the density of the WO₃ films, the H₂ and O₂ concentrations in the gases, thickness of the catalyzing materials and relative humidity. The investigations on the influence of these variants on gas-chromic effect of these samples are underway.

4. Conclusions

An USP technique has been employed to deposit good quality WO₃ thin films. The films after annealing at 400°C for 4 h were substoichiometric, WO_{3-z}. It has been shown that the resistivity and transmittance of USP-WO₃ films with platinum as a catalyzing material presents reversible changes in presence of H₂ and O₂ containing

gases. It is concluded that the samples exhibit relatively slower colouration and bleaching response but higher sensitivity to H₂ and O₂ containing gases.

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