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# $H_2$ sensors based on $WO_3$ thin films activated by platinum nanoparticles synthesized by electroless process

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ABSTRACT

Platinum (Pt) nanoparticles were successfully synthesized on tungsten oxide ($WO_3$) thin films by electroless process without any further post-treatment. The prepared Pt nanoparticles were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and field-emission scanning electron microscopy. Gas sensors based on the Pt–$WO_3$ films were found to provide repeatable and significant responses to ppm-level $H_2$. The size of Pt nanoparticles increases with the deposition time and has improved the sensing characteristics of the sensors. The work in this paper paves a facile way to the fabrication of Pt nanoparticles on metal oxide surface at a low temperature (68 °C).


## 1. Introduction

Hydrogen ($H_2$) is one of the most important energy sources, which is clean and renewable. However, it is also known to have combustible and explosive properties and a high tendency to leak through containers or pipe lines due to its small molecular size. Therefore, there is a strong interest in the development of $H_2$ sensors [1–5]. Among different sensors, $H_2$ sensors based on semiconductor metal oxides are very promising. Noble metal (e.g., Pt, Pd) activated metal oxide sensors show quick responses to $H_2$ due to the fact that noble metal clusters promote the dissociative adsorption of $H_2$ which is an important step in the surface reaction. In this context, the deposition process and the dispersion of noble metal particles on metal oxide surface are of great importance for the sensing properties of the finally obtained sensors.

$WO_3$ is often used as a sensing material for oxidizing gases, e.g., $NO_2$ [6–8] and $O_3$ [9,10]. $WO_3$ interacts with $H_2$ very slowly [11] whereas noble metal activated $WO_3$ is a promising sensing material for low-concentration $H_2$ detection [12–16]. The noble metal catalysts can be added onto the $WO_3$ surface using simultaneous or post-deposition methods. The simultaneous deposition process allows obtaining the $WO_3$ and noble metal particles in one step, e.g. co-sputtering process [13]. The post-deposition method prepares noble metal particles onto the surface of a pre-deposited $WO_3$ layer [14]. The previous works [13,14] showed that the Pt–$WO_3$ films prepared by co-sputtering or dip-coating exhibited good

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responses to $H_2$ after thermal treatments. Nevertheless, a thermal treatment (≥450 °C) is mandatory for preparation of Pt nanoparticles when using these techniques. The thermal treatment may be a disadvantage for certain sensors whose components cannot bear such high temperature treatments, e.g., optical fiber sensors with Bragg gratings [17] or polymer sensors [18,19].

Electroless deposition process uses only one electrode and no external source of electric current. The solution for the electroless process needs to contain a reducing agent to accomplish reduction reaction. A major benefit of this approach is that no power source is required; consequently the cost of production can be significantly reduced and the substrate can be an electrical insulator. Electroless was used to deposit Pt films on the surface of metals and conductive oxides, e.g., titanium [20] and indium tin oxide [21]. It was also reported that Pd particles were deposited on $WO_3$ [22] and amorphous alumina membrane [23] by electroless. However, the preparation of Pt nanoparticles by electroless process on metal oxide surface, e.g., $WO_3$, is less reported. In this work, we report the synthesis of Pt nanoparticles on $WO_3$ thin films using electroless process. The novelty of this paper lies in the preparation of Pt nanoparticles by electroless process without any post heat-treatment. The Pt nanoparticles were characterized and $H_2$ sensing characteristics of the sensors based on the Pt nanoparticles activated $WO_3$ films were studied.

## 2. Experimental method

$WO_x$ films were deposited by radio-frequency (r.f.) sputtering on $Al_2O_3$ substrates fitted with interdigitated Au electrodes on one side and a Pt heater on the other side. The Ø40 mm target was obtained by pressing $WO_3$ powders and sintering them at 900 °C for 1 h. The distance between the substrate and the target in the sputtering chamber was 75 mm and the r.f. power was 200 W. The pressure in the chamber during deposition was 2 Pa, with a gas composition of 90% Ar and 10% $O_2$. The film thickness was measured using an optical profilometer on films sputtered on reference glass substrates. The thickness of the films was 400 nm. After deposition, the $WO_x$ films were annealed at 700 °C in air to convert amorphous $WO_x$ to monoclinic $WO_3$.

The Pt nanoparticles were synthesized on the $WO_3$ surface using electroless process. Firstly, the $WO_3$ films are immersed into a $SnCl_2$ solution at room temperature, to adsorb $Sn^{2+}$ ions on the $WO_3$ surface. After rinsing with distilled water, the $WO_3$ film was then soaked into an activation solution ($H_2PtCl_6$, 1.3 mM) for 5 min at room temperature. This step is used to form Pt nuclei on the $WO_3$ surface through a partial reduction of $PtCl_6^{2-}$ by $Sn^{2+}$. The activated $WO_3$ film was then dipped for 30, 60 and 120 s in a plating solution ($H_2PtCl_6$, 2.6 mM) with hydrazine hydrate solution ($N_2H_4{\cdot}H_2O$, 1.5 mM) at 68 °C. At last, the Pt–$WO_3$ films were rinsed with distilled water at 68 °C and dried at room temperature. The last step ensures the removal of the remaining $H_2PtCl_6$ on the $WO_3$ surface.

Surface morphology of the Pt–$WO_3$ films was inspected by field-emission scanning electron microscopy (FE-SEM). XRD analysis on the films was recorded by an X-ray diffractometer using Cu $K_\alpha$ radiation. $2\theta$ scanning rates of 5° $min^{-1}$ for the range from 10 to 90° was used during the test. In order to characterize the chemical composition, XPS using a monochromatic Al $K_\alpha$ excitation source (1486.6 eV) (Physical Electronics PHI 5600 LS) was used to investigate the core-level excitation of Pt4f for the films at emission angle of 45°. Gas sensing measurements were carried out in a Teflon chamber with $H_2$ concentration ranging from 25 to 200 ppm. More details about gas sensing measurement were given in the previous paper [13]. All the sensors in this work were directly stabilized at 250 °C for 24 h in ambient air prior to the gas sensing tests.

## 3. Results and discussion

Fig. 1 presents XRD patterns of as-sputtered $WO_x$ and annealed $WO_3$ films. The peaks in Fig. 1a belong to the $Al_2O_3$ substrate and Au electrodes. $WO_3$ peaks are not observed in the as-sputtered $WO_x$. After annealing, the as-sputtered films are transformed to well-crystallized $WO_3$. The Pt–$WO_3$ films were also measured by XRD (the pattern is not given). The patterns of Pt–$WO_3$ films are the same to that of the annealed $WO_3$ film. Due to small concentrations (bulk concentration) of Pt in the Pt–$WO_3$ films, it is impossible to detect Pt by XRD.

From XPS survey spectrum of the 30 s Pt–$WO_3$ films as shown in Fig. 2, no peak of Cl is detected, indicating that $H_2PtCl_6$ is completely reduced by hydrazine hydrate, or at least no residue of $H_2PtCl_6$ is present on the surface of Pt–$WO_3$ film. From the Pt4f core-level XPS-spectra shown in Fig. 3, it can be found that the main $Pt4f_{7/2}$ and $Pt4f_{5/2}$ peaks corresponding to 71.0 and 74.3 eV are generated by photoelectrons emitted by metallic Pt. At the meantime, there are small peaks belonging to $Pt^{2+}4f$ and $Pt^{4+}4f$, which may be attributed to the oxidation of Pt nanoparticles. The results showed that the chemical compositions of platinum in the three films are almost the same, and the spectra of 30 s and 120 s Pt–$WO_3$ films are given in Fig. 3. The Pt concentration on the $WO_3$ surface was estimated by XPS to be respectively 2.0, 4.2 and 7.8% for 30, 60 and 120 s Pt–$WO_3$ films. It should be mentioned that XPS is a surface analysis technique, which detects only electrons

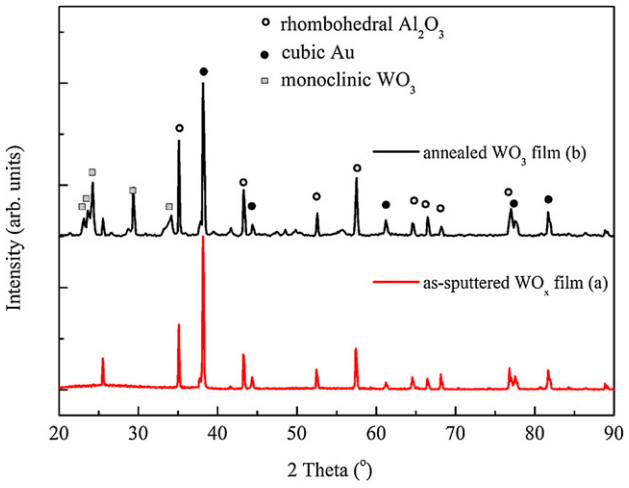


**Fig. 1 – XRD patterns of (a) as-sputtered $WO_x$ and (b) annealed $WO_3$ films.**