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Gas sensitivity of sol-gel prepared mesoporous WO_3 thin film

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Abstract

Tungsten oxide thin film was prepared by sol-gel method from tungsten hexachloride (WCl_6) precursor material in analytical grade ethanol. In order to form the porous nanostructured WO_3 thin film Pluronic F127 was added to the solution. The sol-gel solution was deposited by spin coating on micro-hotplates containing interdigital platinum electrodes on top to measure the sensing layer conductivity. The porous tungsten oxide films were sensitized with ~20 nm platinum nanoparticles. Sensor responses of pure and sensitized porous WO_3 were measured and their responses for 100 ppm H_2S in synthetic air were compared in the 140-260°C operation temperature range. The presence of platinum nanoparticles significantly increased the sensitivity for H_2S gas. Test results of different operating temperatures were investigated in terms of sensitivity, stability and response time.

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Keywords: tungsten oxide; mesoporous; platinum nanoparticles; gas sensor

1. Introduction

Semiconductor metal-oxide (SMO) thin films are among the most intensively investigated materials for gas sensing devices. The best SMO gas sensors exhibit quick sensing response, simple implementation, low manufacturing cost and have stable chemical and thermal properties over extended period. A large variety of deposition methods has been proposed to prepare thin films, such as spray pyrolysis, physical vapor deposition,

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pulsed laser deposition, sol-gel technique, etc [1]. As the thickness of space charge layer at the crystal surfaces plays crucial role in the nano-porous material, these layers are more sensitive than the compact grain structured thin films. Moreover, the high surface-to-volume ratio enhances the sensing area and the gas easily diffuses through the surface into the bulk. In contrary, the gas can not diffuse in the compact grain structured materials. It is well-known that addition of nano-sized catalyst, such as noble metals typically enhances the gas sensitivity of the thin layer. In this work we prepared non-doped and platinum sensitized mesoporous WO_3 thin films by sol-gel technique and investigated the effect of Pt on gas sensing properties.

2. Experimental

2.1. Mesoporous WO_3 thin film

The WO_3 thin films were synthesized by sol-gel technique. Different amount of Pluronic F127 block copolymer were dissolved in 10 ml analytical grade ethanol. 1g tungsten hexachloride (WCl_6) powder was added to the solution and stirred for 1h, followed by ageing for another 24h at room temperature [2]. The WO_3 sol was transferred onto the surface of the micro-hotplates by spin-coating technique (2000 rppm). Combined with lift-off technique, sensing layers of 75 μm diameter and 150 nm thickness were formed on the top of the hotplate. Applying 5 °C/min ramp up heating the sensors were annealed at 300°C, 400°C and 500°C in air for 90 minutes to form the final mesoporous structured WO_3 layers (Fig. 1a.). Finally, the chips were exposed to O_2 plasma treatment (P=400 W, t=5 min) to remove the residues of solvent and all organic ligands.

2.2. Platinum nanoparticles sensitized WO_3 thin film

3.6 ml of a 0.2 M solution of chloroplatinic acid hexahydrate was added to 46.4 ml of boiling distilled water. After 1 min, 1.1 ml of 1 M sodium citrate solution was added, then 0.55 ml freshly prepared sodium borohydrate (0.08 M) solution containing 1 M sodium citrate was quickly injected. After 10 min the product was cooled down to room temperature**.** These nano-particles were used as seeds to grow the larger (~20 nm) particles. 1 ml of the platinum seed solution was dissolved in 29 ml distilled water at room temperature and mixed with 0.045 ml of a 0.4 M chloroplatinic acid hexahydrate. This solution was mixed with 0.5 ml 1 M sodium citrate and 1.25 M L-ascorbic acid. Under stirring, the temperature was slowly increased to the boiling point (~10 °C/min) [3].
The synthesized platinum (~20nm) nano-particles were dropped onto the above described WO_3 sensing layer onto the middle of the membrane. Finally, the sensors were annealed at 300°C for 15 minutes and exposed to O_2 plasma treatment (P=400 W, t=5 min) to remove the solvent and to form separated platinum nanoparticles on the WO_3 films (Fig. 1b,c).

3. Results

The micro-sensor is built on a sandwich structured, non-perforated membrane with embedded Pt heater and Pt interdigitated electrodes on top. The comb-like Pt electrodes serve for measuring the resistance of the sensing layer. The membrane was released by deep reactive ion etching of Si underneath. The Pt filament and the Pt interdigitated electrodes were positioned in the middle of the membrane.
The obtained WO_3 thin layers have different porosities due to the different concentrations of the F127 surfactant molecule. The WO_3 films were annealed at different temperature to remove the Pluronic block copolymer to get the porous thin layer. In order to prepare WO_3 films of the best porosity we optimized these last two parameters (F127 concentration and annealing temperature). Fig. 1a shows that the highest porosity is provided by solution containing 1g F127 if annealed 300°C. The WO_3 layer looses its integrity and cracks if the annealing temperature exceeds 300°C.

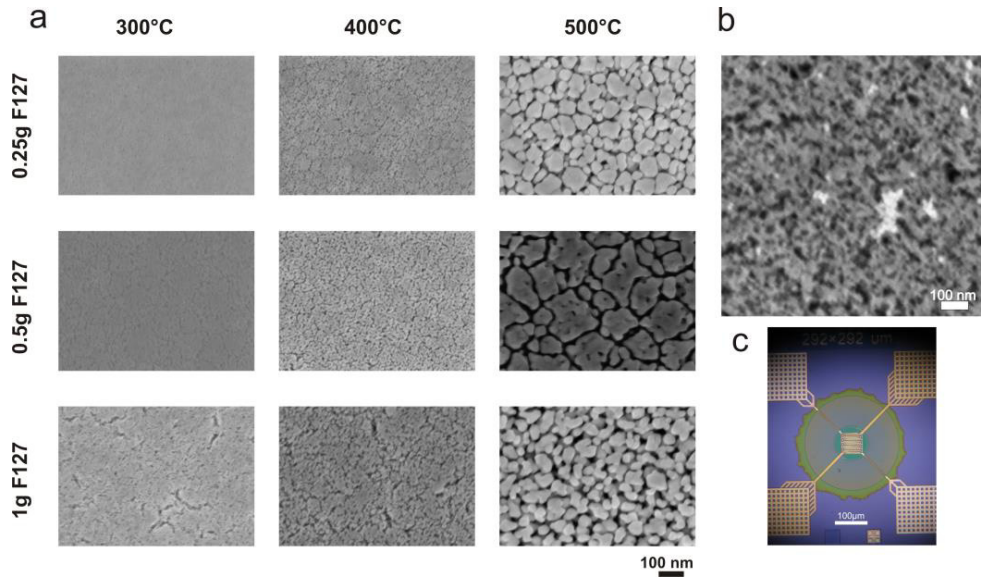

Fig. 1. (a) SEM images of WO_3 layers with different porosity and annealing temperature; (b) SEM image of platinum sensitized porous WO_3 thin film; (c) Image of the gas sensor device.

Sensors were tested for 100 ppm H_2S in synthetic air at operating temperature range between 140-260°C. For 100 ppm H_2S the sensitivity of the bare and Pt activated sensors continuously increases with the operation temperature (Fig. 2).

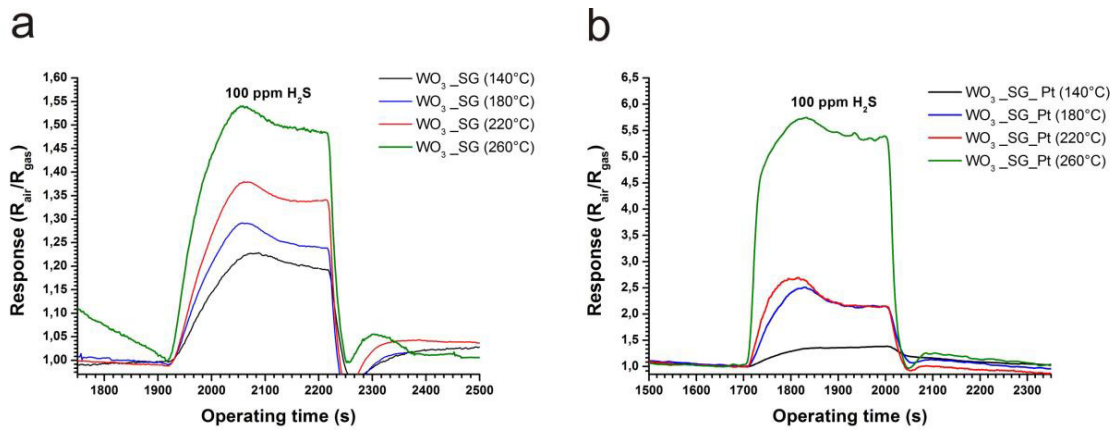

Fig. 2. (a) Sensors signal of porous WO_3 film for 100 ppm H_2S at different operating temperatures; (b) Sensor response of Pt nanoparticles doped porous WO_3 for 100 ppm H_2S at different operating temperatures.

The sensitivity of the platinum treated WO_3 sensor is significantly higher. In this case the effect of platinum nano-particles is obvious: the catalyst sensitized sensors deliver approximately 4 times higher response at 260°C as compared with the non-doped reference (Fig. 3). The other positive effect of the noble metal particles is definite

when envisaging the response time: the ca. 200 sec of the non-doped material is reduced to around 30-40 sec for the doped layer and provides reliable signal. However, less significant difference was found for the recovery times. The 60 sec long recovery of the bare mesoporous WO_3 was slightly reduced to approximately 30 sec for the Pt doped sensor.

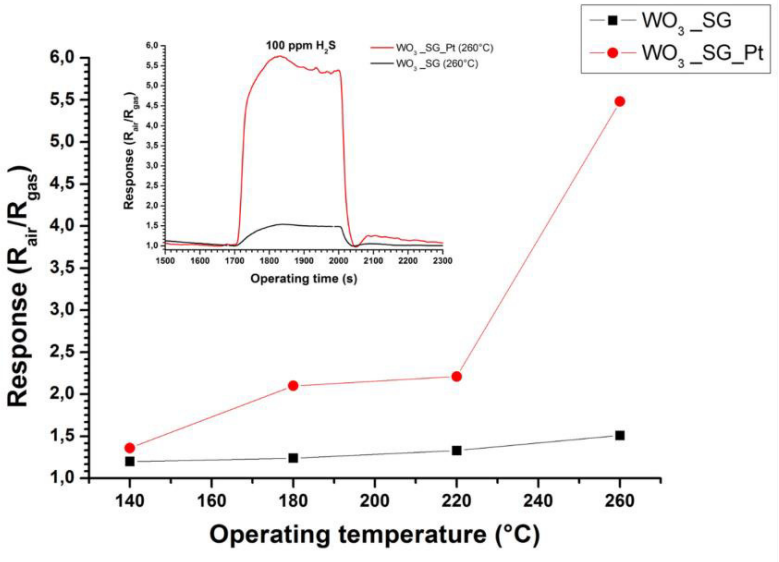

Fig. 3. Sensitivity of pure and platinum activated porous WO_3 layers. Measured in 100 ppm H_2S gas at different temperatures.

4. Conclusion

The performance of non-doped and platinum sensitized WO_3 thin film sensors were tested for 100 ppm H_2S response in synthetic air in the operating temperature range of 140-260°C. Platinum nano-particles were added to the sol-gel synthesized mesoporous WO_3 thin film to form the sensing layers. Pt doped sensors exhibit four times higher sensitivity and quicker response/recovery time for H_2S. Moreover, the sol-gel formed sensing layers exhibit better reproducibility. The effect of humidity as well as detection of NO_x and NH_3 will be the subject of further investigations.

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