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Study on Gas Sensing Properties of WO_3 Thin Films

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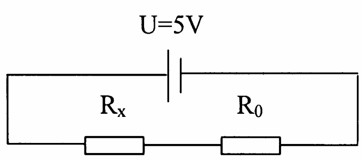
Abstract. Tungsten oxide thin films were prepared by an inorganic-sol-gel dip-coating process, where the sol was obtained by adding citric acid, as chelating agent, to the ammonia solution of tungstic acid. The resultant thin films were a mixture of monoclinic and tetragonal phases of WO_3 and, after being pretreated at 600°C and sintered at 650°C, the average grain size of the polycrystalline films was about 500 nm. The gas-sensing properties of WO_3 thin films were tested at temperatures ranging from 500° to 600°C and in nitrogen gas containing 5vol% O_2 or 5vol% H_2. The WO_3 sensors exhibited a good sensitivity and response speed at the temperature of 550°C.

Introduction

It has been a long time that the semiconducting metal oxides thin films such as SnO_2, TiO_2, ZnO, and WO_3 were used for gas sensors [1,2]. The working mechanism of these gas sensors can be described as the changes of the oxide film resistance resulting from physisorption, chemisorption, and catalytic reactions of the gases in the surface of the film. It's well known that Tungsten oxide (WO_3) is a n-type semiconductor which has been reported to have promising electrical and optical properties for various applications like efficient photolysis, electrochromic devices, selective catalysts and gas sensors [3]. It has been noted that WO_3 shows a good property for gas sensing to various gases such as H_2S, NO_x, trimethylamine and a number of other organic compounds gases. Especially WO_3 has been reported to be the most promising material as NO_x sensor even at low and elevated working temperature [4]. The semiconducting metal oxide thin films and thick films were uesd for gas sensing materials since they were proved to be more sensitive than bulk ceramics [5]. In comparing with thick films, thin films exhibit higher gas sensivity and faster response time. The thin films can be fabricated by techniques such as vacuum vaporization, chemical vapor deposition and sol-gel method. Sol-gel method can easily control the film structure and introduction of dopants by changing the composition of solution, and has a low process cost than other techniques. So the present work prepared WO_3 thin film based on the inorganic sol-gel (ISG) method. An excellent sensing property had been achieved to the small quantities of H_2-O_2 in the environment atmosphere of N_2. It's also noted that the doping of noble metal in the surface of WO_3 thin film would greatly enhance the gas sensing property.

Experimental

Preparation of WO_3 thin films. WO_3 thin films were manufactured by a sol-gel dip-coating method: citric acid and tungstic acid with the ratio of 1:1 were dissolved in 20ml ammonia, then stirred at 80°C utill the solution color changed from yellow to transparent and the final concentration of aqueous solution was 0.2M. WO_3 thin films were deposited on the alumina substrates with a dimension of 15 × 10 mm. The coating process was performed by dipping the substrates into the solution and withdrawing at a speed of 4.6~4.8 cm/min, then the liquid solution was coated on the substrate surface uniformly. The sol films were dried at 120°C for 10 min to remove the water, and were put in the furnace under the temperature of 600°C for 20 min to transform the precusor gel into WO_3. After 10 dip-coating-heat-treatment cycles, the thin films were finally sintered at 650°C for 30 min.



R_x: WO_3 thin film
R_0: Sampling

Fig. 1 Circuit for testing gas sensing property

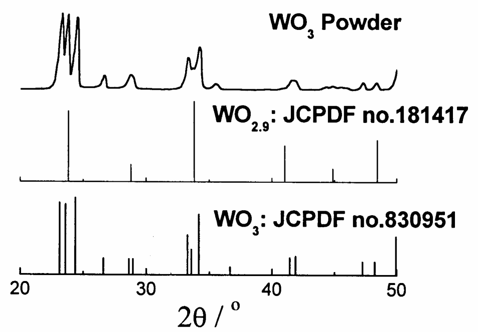


Fig. 2 XRD pattern of WO_3 powder sintered at 650°C

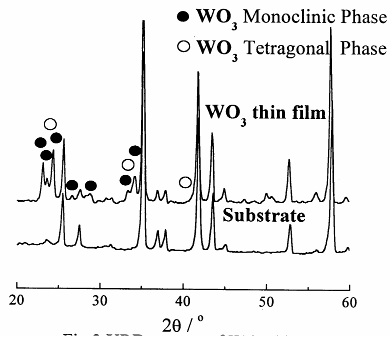


Fig.3 XRD pattern of WO_3 thin film sintered at 650°C

Characterization. The surface morphology was characterized by scanning electron microscope (SEM) and the crystalline phase was analyzed by X-ray diffraction (XRD) with a Cu Kα source. In order to measure the gas sensitivity of WO_3, the thin films were placed in a quartz tube which could be heated up to 800°C. The mixed gas of hydrogen, oxygen and nitrogen could provide oxidizing or reducing atmosphere. The flow rate of the testing gas could be controlled by mass flow controller equipment. The electric circuit for measure the changes of thin films resistance was shown in Fig.1. The voltage of fixed resistance R_0 was measured by a computer data-collecting system, so the resistance of thin films R_x connected to R_0 was calculated.

Results and Discussion

Characterization of the thin films. Phase identification based on X-ray diffraction results was shown in Fig. 2. The crystalline structure of WO_3 powder was confirmed as ReO_3-type oxide with a slight distortion prepared by the thermal decomosition of the complex precusor gel at 650°C [6]. Three most intense diffraction peaks were located at 2θ angles of 23.15°, 23.59° and 24.40° respectively, which were identified with JCPDS number of 830951 for monoclinic phase. Moreover, another intense diffraction peak could be observed at 2θ angles of 23.74°, which was identified with JCPDS number of 181417 for tetragonal phase. So the WO_3 powder prepared by sol-gel method showed a mixture of two phases of tetragonal and monoclinic. It could be observed from Fig. 3 that the X-ray diffraction patterns of thin films sintered at 650°C showed a mixture of monoclinic and tetragonal phases as the same to the WO_3 powder.

Fig.4 revealed the microstructure of the dipped films calcined at 650°C for 30min: the average grain size was about 500 nm, and the film pocessed somewhat high porosity which originated from the decomposition of the organic compound during the sintering process. The influence of the specific porous microstructure greatly increased the surface area of WO_3 thin films on the substrate, which had an important effect on the gas sensing properties [7].

Oxygen-sensing properties of WO_3 thin film. The gas sensing mechanism of gas sensors is that as the solid adsorbs more electronegative gas, the solid lose electron to the gas, causing a space charge layer (or depletion layer) formed near the surface where the uncompensated donor ions survive. WO_3 is an n-type semiconductor, so the resistance of the thin films go up in an oxidizing atmosphere and fall down in a reducing atmosphere. The sensitivity of thin films could be defined as: $S = R_{ox}/R_{re}$, where R_{ox} is the resistance of the thin films in the oxidizing atmosphere, while R_{re} is the resintance in the reducing atmosphere. In this investigation, the response time was the time that defined as the period in which the output voltage changed from 10% to 90% or vice versa.

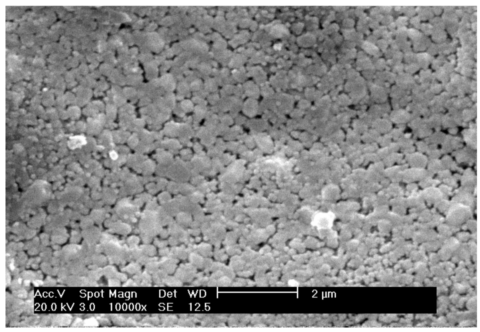


Fig.4 SEM photograph of thin film sintered at 650°C

Fig.5 presented the dynamic output voltage curves of WO_3 thin films fired at selected temperatures in the range

600 ~ 700°C, exposed to H_2 (5% in volume) and O_2 (5% in volume) alternately in N_2 atmosphere at the operating temperature of 550°C. One can observe that the response time was in the order 650°C < 600°C and 700°C, which meaned the films sintered at 650°C had a higher gas-sensing properties. Either decreasing or increasing the calcination temperatures would lead to the deteriorating of response speed. Fig. 6 showed the influences of testing temperature and sintering temperature on the sensitivity of thin films. The sensitivity were also strongly affected by the sintering temperature, where the sensitivity of sample sintered at 650°C was higher than those sintered at 600°C and 700°C at the working temperature range from 500°C to 600°C. All the above results can be explained in terms of the characteristic of WO_3 thin films. For calcination temperatures lower than 650°C, the main crystalline phase was monoclinic structure. Solis et al stated that the tetragonal phase was responsible for the gas sensing properties of WO_3[8]. However, increasing clcination temperature higher than 650°C would result in the increase of the grain size, consequently the decrease of surface area. Therefore the adsorption of gas molecules was relatively low, and it was possible a factor for decrease of gas sensitive. In our work, we defined the most optimum sintering temperature was 650°C.

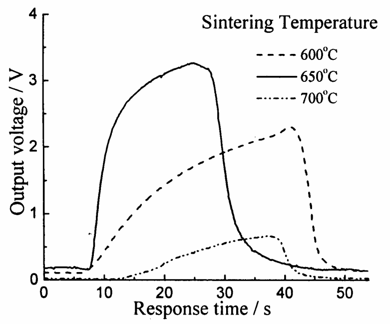


Fig.5 Gas response characteristic of the WO_3 thin film at 550°C

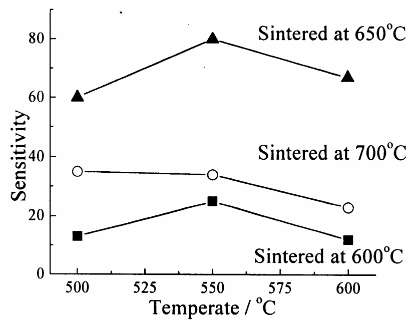


Fig.6 Oxygen sensitivity of thin film sintered under different temperatures

According to Fig. 6, the sensitivity of thin films sintered at 650°C was a function of the operating temperature, and it reached a peak value of 80 at 550°C. When the temperature was increased or decreased, the sensitivity became lower. Since the gas-sensing machenism of WO_3 thin films can be considered as the reaction between the adsorbed oxygen and hydrogen:

$$2H^{+}_{ads.}+O^{2-}_{ads.}=H_2O \quad (1)$$

the situation of gas adsorption or desorption in thin films surface and the thermally activated reaction energy would play an important roles. At lower operating temperature than 550°C, the actived energy caused by temperature were not enough for the Eq. 1, but at a higher temperature, it was due to the gas desorption became significant, then the surface coverage by adsorbed gas was reduced, which were the reasons of sensitivity depended on temperature effect.

Oxygen-sensing properties of Pt doped WO_3 thin film. Although thin films based on WO_3 had proved to be suitable for prepared the gas sensor, they still suffered from a lack of sensitive in practical applications. It could be noted that the most rapid response time of WO_3 thin films sintered at 650°C was 8.8s and 6.4s respectively response to to H_2 and O_2. The sensing properties of WO_3 thin films could be improved by adding certain noble metal to its surface, since the adsorption ability of oxygen or hydrogen could be increased in the metal-oxide. For example, under the oxidation atmosphere, the resistance was dominated by tunneling between discrete metal particles on a charged metal-oxide surface, oxygen adsorption increased the electrostatic barrier and the WO_3 thin films resistance, and then the removal of oxygen due to desorption would restore the original metal-oxide resistance[9]. In this paper, we reported the effects of surface modification of Pt on the gas-sensing properties. The WO_3 thin films were soaked in chloroplatinic acid for 12h, and then dried at 120°C, sintered at 650°C for 30 min. The measuring results of doped sample were shown in Fig. 7 and Fig. 8. It was found that the sensitivity increased sharply compared with the pure WO_3 thin films: the sensitivity changed from 360 at 550°C to 4100 at 600°C. At the same time, the response speed was also accelerated: the time reduced to 3.3s at 550°C and 0.3s at

600°C for H_2, and for O_2, the response time decreased from 16.9s at 550°C to 1.2s at 600°C. So the doping of Pt on WO_3 surface greatly improves the sensing property of thin films.

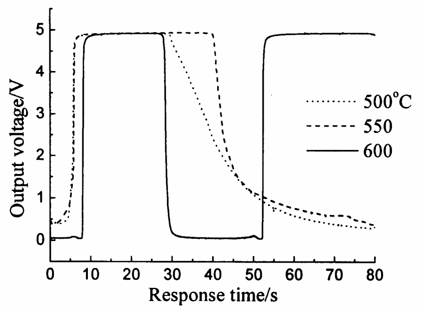


Fig.7 Oxygen sensitivity of WO_3 thin films doped by Pt under different temperatures

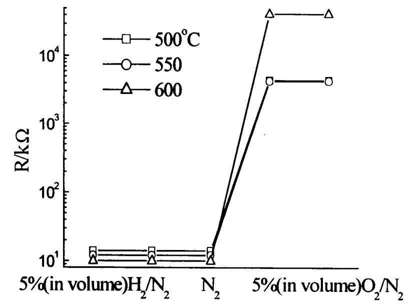


Fig.8 Oxygen sensitivity of WO_3 thin films doped by Pt under different temperatures

Conclusions

WO_3 thin films were prepared by inorganic-sol-gel dip-coating method using tungstic acid as raw material and adding chelating agent of citric acid. The XRD analyses indicated that both the powder and thin films acquired were a mixture of monoclinic and tetragonal phases of WO_3. From all the experimental results shown above, we concluded that due to its porous microstructure, the WO_3 thin films had a good sensitivity and response speed. The gas sensing properties were greatly depend on the sintering temperature and the operating temperature, for pure WO_3 thin films after fired at 650°C, a tested temperature of 550°C exhibited the fast response time. Moreover, modifying WO_3 thin films with Pt had a dramatic influence on the gas sensitive properties, the sensitivity could reach three order of magnitude and the response time could reduce to about one second.

Acknowledgement

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