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NO-Sensing Characteristics of Pure and Pt-Doped WO_3 Films Prepared by Sol-Gel Technique

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Abstract: Pure and Pt-doped ($m(Pt):m(WO_3) = 0.3\%$) WO_3 thin films were prepared using the sol-gel process by the dip coating technique on alumina substrates. The resistance of pure and Pt-doped thin films fired at various temperatures in the range of 450 – 850?℃ were measured and compared. An optimum sintering temperature was judged to be 650?℃. The pure WO_3 thin films maximum sensitivity to 40×10^{-6} NO was 8.9 at optimum operating temperature 350?℃. Maximum sensitivity of the Pt-doped ($m(Pt):m(WO_3) = 0.3\%$) WO_3 thin film's to 40×10^{-6} NO was 114.0 at optimum operating temperature 250?℃. The experimental results demonstrated that Pt-doped WO_3 thin films obtained by sol-gel technique have high sensitivity, low operating temperature, fast and reproducible response to NO.

Key words: nitric oxide, WO_3, sol-gel, Pt, thin film

Tungsten oxide is considered as one of the best candidates for nitrogen oxide (NOx)[1-3] detection. Though a large number of papers have been published on the use of WO_3 films for the detection of NOx, few make a clear distinction between the response towards NO and NO_2. The reason is that NO can react very rapidly with oxygen and photoassisted reaction is well known. Nitric oxide (NO) as a combustion by-product associated with air pollution is recognized as playing a critical role in the ever increasing of diseases[4]. The detection of NO is very important.

WO_3 films have been prepared using various techniques such as thermal evaporation[5], sputtering[2], chemical vapor deposition[6]. Recently, the sol-gel process has been proposed as a new technique for preparing films[7]. Sol-gel technology is well suited for production of thin film sensors (the film thickness is typically less than 1?μm) because of its relatively low processing cost and the ability to control the film morphology. Sol-gel technology is easy to modify the composition with uniformly dispersed additives due to the starting materials mixed on the molecular level. Although the sol-gel technique has been widely used for the preparation of powders, the potential of this technique for application to the thin film sensor has not been fully explored.

In this paper, we emphasize the preparation of pure and Pt-doped WO_3 thin films through dip coating by the sol-gel technique. The resistance of pure and Pt-doped thin films fired at various temperatures in the range of 450 – 850?℃ was measured and compared. The response of the films to NO was investigated and reported. The sensing mechanism was discussed as well.

1 Experiment

1.1 Thin film preparation and structural characterization

Ammonium metatungstate was obtained from Aldrich. Hexachloro-platinate ($H_2PtCl_6 \cdot 6H_2O$) was received from Beijing Chemical Factory. Pure WO_3 sols (5.0%) were prepared as follows: powder of ammonium metatungstate was added into ethanol (95%), together with a trace amount of HCl solution. The solution was stirred until it became viscous. For the preparation of Pt-doped sols, with $m(Pt):m(WO_3) = 0.3\%$, the prescribed amount of $H_2PtCl_6 \cdot 6H_2O$ was directly dissolved in ethanol containing prescribed ammonium metatungstate. With this procedure clear and homogeneous sols (pure WO_3 sols and Pt-doped WO_3 sols) were obtained. No precipitation was observed.

The films, with thickness about 120 nm, were deposited on 15?mm × 20?mm Al_2O_3 (250?μm in thickness) substrates for electrical characterization. For film formation we used the dip coating technique.

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The yield of deposition is dependent on the viscosity. Alumina substrates were dipped and immersed into the WO_3 sols (or $m(Pt):m(WO_3) = 0.3\%$ sols). After a few minutes, the samples were withdrawn upward and vertically relative to the solution surface with a speed of 5.0?mm/s, then the films were dried at 80?℃ for 0.5?h. The samples were obtained by repeating film deposition and drying treatment five times. The final films were fired 1?h in air at various temperatures ranging from 450?℃ to 850?℃ in an electrical furnace.

Because thermal analysis (Perkin-Elmer, TGA6) facility was not equipped with accessories for making measurements on thin films, some investigations were performed on powders. Powders were prepared from the sols by evaporating the solvent at 100?℃ in air. TG (DTG) analysis was carried out in the 30 – 800?℃ temperature range, with a heating rate of 10?℃/min in dynamic air.

1.2 Electrical and gaseous characterization

Two Ag electrodes were deposited on the surface of the film, which made ohmic contact with the film. The film was assembled on a heating bed inside a glass chamber (100?mL) equipped with a gas inlet and outlet. The films were kept at a chosen temperature with range from 150?℃ to 400?℃ and the temperature was measured by chromel-alumel thermocouple. The electrical characteristics of films were obtained by measuring the electrical voltage under constant current and a multi-meter (HP3457A) was used to measure resistance of the films. Gases were controlled by mass flow meters. Experiment was automated and controlled through a computer by means of IEEE interfaces and DASTLab5.0 software.

The gas sensing properties of pure and Pt-dopted WO_3 films were evaluated based on the following parameters: sensitivity (S) is defined as R_{NO}/R_{air}, where R_{NO} and R_{air} are film resistance in air mixed with NO and in pure dry air, respectively. The sensing response to NO was measured in the range of 150 – 400?℃. Different gas compositions were obtained by diluting NO with dry air.

2 Results and Discussion

Fig.1 shows the TG and DTG curves coming from measurements performed on pure WO_3 powders. First mass loss region is observed at temperature 100?℃. This can be attributed to desorption of water. Another large mass loss region is observed at 250?℃ and is attributed to pyrolysis of the organic residuals in the powders. The two later peaks of DTG curve which appear in the temperature range between 300?℃ and 400?℃ can be attributed to the completion of the organic elimination through their oxidation and to the crystallisation of WO_3, respectively, over which the stability of oxide is confirmed. The curves for Pt-doped powders did not show a different structure with respect to the curves in Fig.1.

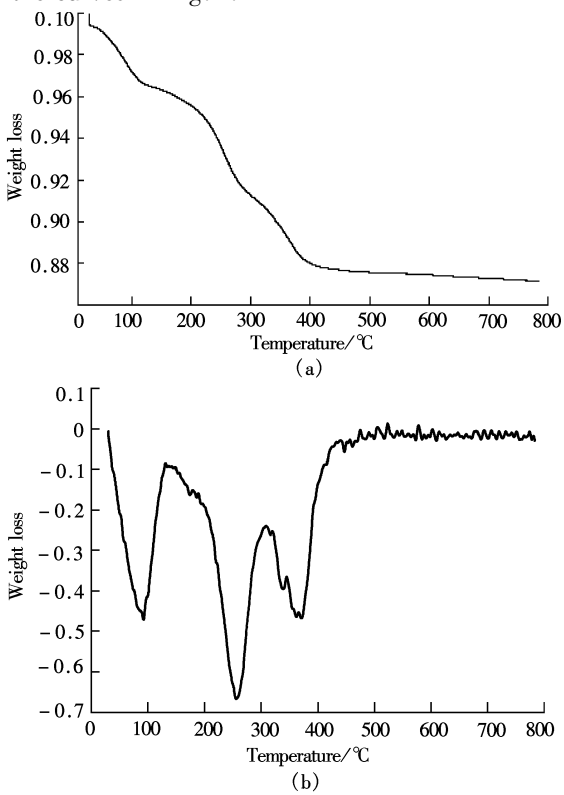

Fig.1 Thermal analysis of WO_3 powder curves. (a) TG; (b) DTG

First of all, we investigated the optimum calcination temperature of the thin films dip-coated from sol solution. From TG and DTG curves we know that the sinter temperature of films must be higher than 400?℃. Fig. 2 shows the electrical resistance in air of pure and Pt-doped thin films fired at various temperatures in the range of 450 – 850?℃ for 1?h. The resistance increased steeply as the sintering temperature exceeded 650?℃. Steep increase in resistance perhaps was due to the crack formation. Based on this, an optimum sintering temperature was judged to be 650?℃.

The values of electrical resistance of pure and Pt-doped WO_3 thin films were measured and compared (sintering temperature 650?℃). Fig.3 shows the electrical resistance of each film in air as a function of

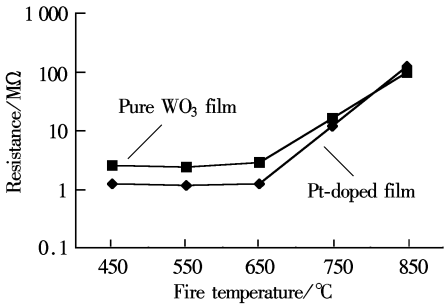

Fig. 2 Resistance in air as a function of fired temperature

operating temperature. The resistance values in air decreased with a rise of operating temperature. This is a typical characteristic of ceramics. The Pt-doped samples show higher resistances, which corresponds to a high grain barrier. This increase of the grain barrier maybe due to higher oxygen adsorption at the grain interface enhanced by a higher density of semiconductor adsorption sites introduced by the presence of platinum, or may be directly related to platinum clusters localized at the grain interface[8].

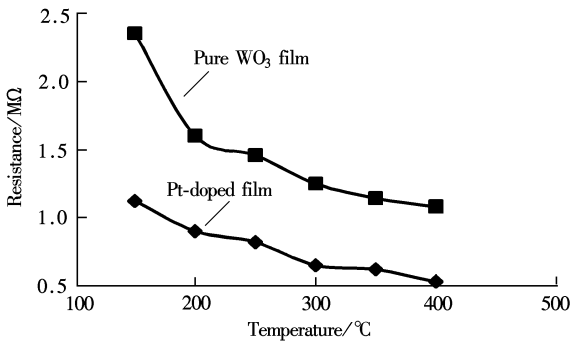

Fig. 3 Resistance in air as a function of operating temperature (sintered at 650℃)

In the case of tests in NO atmosphere the samples were placed in a glass test cell where the electrical resistance was continuously detected automatically. The response was studied in a temperature range from 150?℃ to 400?℃. At each temperature, before starting measurements the films were kept under dry air flow and were allowed to equilibrate until the computer-monitored electrical resistance was constant vs. time. Changes in the electrical resistance resulting from the nitric oxide adsorption were measured on both pure and Pt-doped WO_3 films. Here we report some of the most relevant experimental results obtained with samples prepared by heating at 650?℃.

Fig.4 shows the dependence of sensitivity on operating temperature of both pure and Pt-doped WO_3 thin films in 40×10^{-6} NO gas. It is evident that the sensitivity of Pt-doped WO_3 varies with operating temperature in a different way from that of pure WO_3. The sensitivity for the pure WO_3 thin film towards NO is very low. Fig.4 shows that the sensitivity of pure WO_3 films to NO increased with rising temperature up to 350?℃, and decreased when the temperature is higher than 350?℃. Thus, the pure WO_3 exhibited an optimal sensitivity to NO at temperature around 350?℃. In constract, the Pt-doped WO_3 films exhibit better sensitivity in all operating temperature, and the optimum operating temperature was found to be 250?℃. It can be seen that the additives of Pt enhance the sensitivity of films and reduce the optimum operating temperature.

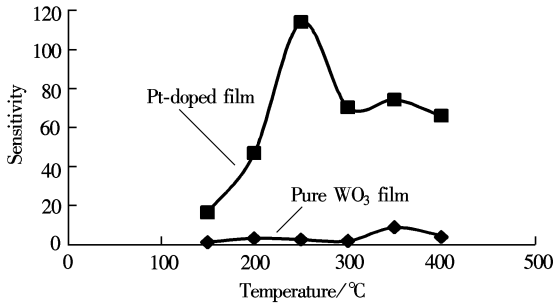

Fig.4 Variation of sensitivity to 40×10^{-6} of NO with operating temperature for pure and Pt-doped WO_3 films (fired at 650?℃)

Fig.5 shows the dependence of sensitivity on the concentration of nitric oxide for pure and Pt-doped WO_3 films at operating temperature of 350?℃ and 250?℃, respectively. The sensitivity increases linearly with the accretion of NO concentration when concentration increased from 5×10^{-6} to 40×10^{-6}. Fig.6 shows the dynamic response of the Pt-doped WO_3 film to square pulses of NO (5×10^{-6}, 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6}) at a working temperature of 250?℃. The response and recovery time (time for 90% of resistance change) were 3?min and 5?min for NO/air mixture in a $5 \times 10^{-6} - 40 \times 10^{-6}$ range, respectively.

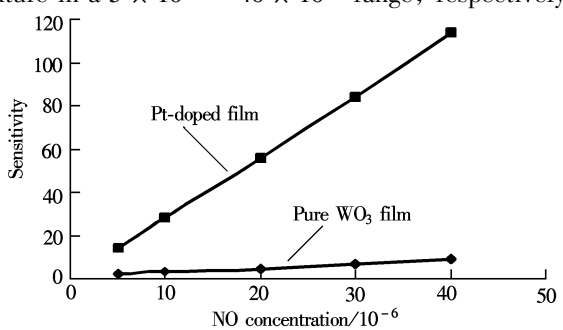

Fig.5 Calibration curves of pure (operating temperature, 350?℃) and Pt-doped (operating temperature, 250?℃) WO_3 film fired at 650?℃ for 1?h

The response and recovery times depend on the operating temperature, being both slow at lower temperatures and fast at higher temperatures. The

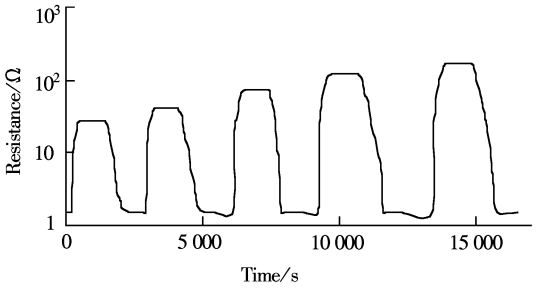

Fig.6 Pt-doped film response (fired at 650?℃ for 1?h) in air and NO/air mixture at 250?℃

Pt-doped film of high sensitivity with short response and recovery time is possible candidate for application like electric nose and breath analyzer.

Sensing properties of films depend mainly on the interactions between the sensing film and the gas to be detected. The interactions include physical and chemical adsorption. Physical adsorption refers to a surface adsorption caused by dipole-dipole or Van der Vaals interactions. Chemical adsorption, on the other hand, involves primary bonding or electrostatic interaction. The chemical interaction typically involves exchange of electrons between adsorbed gas molecules and the sensing film. It results in a change in band bending near surfaces and the electrical property of the sensing film. At elevated temperature, chemical adsorption is dominant. The transition from physical adsorption to chemical adsorption needs activation energy, which can be accomplished by increasing temperature.

We have tested NO sensing properties of pure WO_3 films under different carrier gas. Fig.7 shows the electrical resistance variation of a pure WO_3 film (fired at 650?℃ for 1?h) at 350?℃ both in a flow of dry air and in a flow of helium gas, with a fixed concentration of NO (40×10^{-6}). It is quite evident that both of their responses show similar behavior and so the adsorption mechanism of NO on pure WO_3 films does not involve the oxygen. The sensing mechanism for pure WO_3 is as follows:

$$NO(g) \rightarrow NO(ads)$$
$$NO(ads) + e^- \rightarrow NO^-$$

Therefore, NO behaves as an oxidizing gas, increasing the resistance in *n*-type semiconductor WO_3.

In air, for Pt-doped WO_3 films, oxygen and nitric oxide are absorbed on Pt as well as on the surface of WO_3 grains. The sensing mechanism depends on reaction between oxygen and nitric oxide. Oxygen in the film can be several forms, molecular (O_2^-), atomic (O^-, O_2^-). Because of presence of platinum, NO^- can

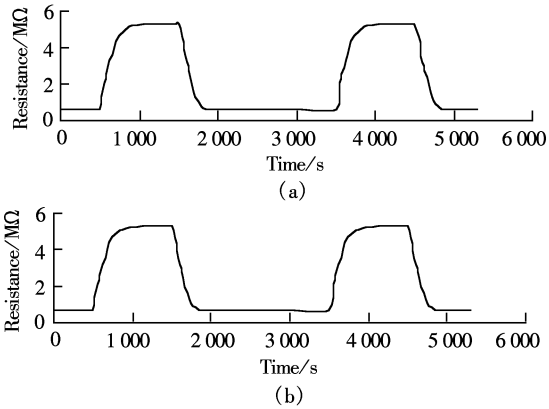

Fig.7 Resistance variation at 350?℃ in (a) dry air and (b) helium under a concentration of 40×10^{-6} NO

react with atomic oxygen (O^-) in the range of the operating temperature.

$$NO(g) \rightarrow NO(ads)$$
$$NO(ads) + e^- \rightarrow NO^-$$
$$NO^- + O^- \rightarrow NO_2$$

In this process, the activation of NO gas molecules to active NO^- is an important step. Pt-doped in WO_3 thin film acted as a kind of catalyst, which can catalyze the reactions of gas phase species with the film surface. It reduces the activation energy in the dissociative chemisorption, which includes the dissociation of chemisorbed oxygen and nitric oxide molecules. This was the reason why the film response (R_{NO}/R_{air}) to 40×10^{-6} NO was enhanced from 8.9 for the pure WO_3 film to 114.0 for Pt-doped WO_3 film. The temperature for maximum sensitivity to NO is 250?℃ for Pt-doped WO_3 films and 350?℃ for pure WO_3. It seems that more energy is needed for NO to grab O^- form the film in the absence of platinum. Apparently, platinum plays an important role in the interaction of NO with sensing materials and desorption of O^-, greatly influencing the speed of response and sensitivity.

3 Conclusion

Pure and Pt-doped ($m(Pt):m(WO_3) = 0.3\%$) WO_3 thin films for NO gas detection were prepared using the sol-gel process by the dip coating technique on alumina substrates. An optimum sintering temperature was at 650?℃. The pure WO_3 film exhibited an optimal sensitivity to NO at temperature around 350?℃. The optimum operating temperature of the Pt-doped WO_3 films was found to be 250?℃. The sensitivity of the pure WO_3 film was much lower than that of the Pt-doped ($m(Pt):m(WO_3) = 0.3\%$)WO_3 thin film. The experimental results demonstrated

Pt-doped ($m(Pt):m(WO_3) = 0.3\%$) WO_3 thin films have high sensitivity, low operating temperature, fast and reproducible response to NO.

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溶胶–凝胶制备的纯和铂掺杂三氧化钨膜的一氧化氮气敏特性

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摘 要 用溶胶-凝胶浸渍技术在三氧化二铝基片上制备了纯和($m(Pt):m(WO_3) = 0.3\%$)铂掺杂的三氧化钨膜.测量和比较了 450 – 850?℃温度范围内不同退火温度的纯和铂掺杂三氧化钨膜的电阻,理想的退火温度为 650?℃.纯三氧化钨膜的理想工作温度为 350?℃,对 40×10^{-6} 一氧化氮的灵敏度为 8.9;铂掺杂三氧化钨膜的理想工作温度为 250?℃,对 40×10^{-6} 一氧化氮的灵敏度为 114.0.实验结果显示溶胶-凝胶制备的铂掺杂三氧化钨膜对一氧化氮具有高的灵敏度,低的工作温度,快速和可重复的响应.

关键词 一氧化氮, 三氧化钨, 溶胶-凝胶, 铂, 薄膜

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