Original Article

In situ construction and sensing mechanism of TiO$_2$–WO$_3$ composite coatings based on the semiconductor heterojunctions

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ABSTRACT

Tungsten oxide (WO$_3$) is one of the most promising gas-sensitivity materials owing to its high decomposition temperature and stability of microstructure. The doping of oxides can significantly improve its gas-sensitivity properties. In this paper, WO$_3$ based coatings doped with TiO$_2$ were prepared via plasma spraying technology by using mixed feedstock suspensions containing a precursor as WCl$_6$ and a certain ratio of nano-TiO$_2$. The characterization of microstructures and properties of the TiO$_2$–WO$_3$ composite coatings were achieved and the gas sensitivity mechanism was researched. During the suspension plasma spraying, the solvent of the precursor droplets was evaporated and then the nucleation, crystallization and growth of WO$_3$ occurred. The crystallinity and crystal grains of WO$_3$ increased observably as the plasma spraying power improved. With the increase of TiO$_2$ in coatings, the average grain size of the TiO$_2$–WO$_3$ composite coatings decreased at first and then increased. And the gas-sensitive properties of the composite coatings were significantly better than the pure WO$_3$ coatings. The gas-sensitive properties improvement of TiO$_2$–WO$_3$ composite coatings doped with TiO$_2$ was firstly caused by the decrease of grains size, which led to an increase of the gas adsorption sites. And the Fermi level effect of the composite metal oxide heterojunction formed by TiO$_2$ and WO$_3$ also markedly enhanced the gas sensitivity properties of the composite coatings.

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1. Introduction

With the requirement of real-time detection of the concentration of harmful gases (NO, NO$_2$, CO, SO$_2$, H$_2$S, etc.) in air, it is
urgent to develop high performance gas sensors in the industrial, environmental and medical fields. The semiconductor gas sensor is one of the most successful commercially applied sensors because of its advantages such as simple structure, long service life, small size and no maintenance [1,2]. The gas sensitive coating is a core part of the semiconductor gas sensor. A variety of materials have been used to prepare the gas-sensitive coatings, such as zinc oxide (ZnO) [3,4], tin oxide (SnO$_2$) [5,6] and iron oxide (Fe$_2$O$_3$) [7,8]. But there are some limitations in these materials such as the low resolution, high power consumption, and instability in certain temperature and humidity. Compared with the traditional materials above [9,10], WO$_3$ has extremely high sensitivity for NO$_2$ detection, and has been an ideal material for gas sensor coatings. And it is also reported that doping another kind of oxides into WO$_3$ leads to the formation of semiconductor heterojunction, thus can effectively improve the gas sensitivity of the coatings.

At present, most of the commercial semiconductor sensors coatings were prepared by screen printing and magnetron sputtering processes. However, the screen-printed coatings displayed a low iterative feature of their structures. And a time-consuming process of high temperature post-treatment was also unavoidable in screen printing (in order to remove the organic binder and improve the bond strength of the coatings) [11–13]. The magnetron sputtering which needed a high vacuum chamber exhibited a slow sputtering rate, a high cost, and an uncontrollable porosity in film [14,15]. Therefore, it was necessarily to develop a high-efficiency and low-cost technique for the preparation of gas sensor coatings. Liquid-phase plasma spraying was an emerging technology for the preparation of coatings with controllable microstructures. The grains and defects sizes in the coatings prepared by liquid-phase plasma spraying were smaller and controllable due to the use of metal salts as precursors. And a larger specific surface area was obtained in these coatings. At the same time, the coatings prepared by liquid-phase plasma spraying showed a higher bonding strength. And there were no need of post-heat treatment and vacuum chamber in liquid-phase plasma spraying. Compare with the traditional technique above, liquid-phase plasma spraying displayed distinct advantages in economizing costs and raising efficiency [16–19]. It is more suitable for the preparation of gas sensor coatings.

It has been reported that doping of metal oxides can significantly improve the performance of WO$_3$ based gas sensors. He [20] sputtered a layer of V$_2$O$_5$ catalyst film on the surface of the WO$_3$ thin film and found that the V$_2$O$_5$ coating with thickness of 20 nm showed a porous structure and an excellent sensitivity. A series of W/Cr oxides (W/Cr = 1:6, 1:2, and 3:2) were prepared by Diao [21]. And one of the oxides with the W/Cr of 3:2 displayed the maximum response ability for NO$_2$ gas in the concentration range of 20–300 ppm. Wang [22] prepared a kind of SiO$_2$–WO$_3$ composite films with SiO$_2$ content between 0 and 20 wt%. It was found that the grain size of WO$_3$ decreased with the increase of SiO$_2$, and the sensitivity of the composite film with 5% SiO$_2$ was much higher than that of pure WO$_3$. It can be seen that improving the gas sensing properties of coatings by doping of metal oxides is a hotspot in recent research. However, the influence of the types and proportions of doped metal oxides on the gas sensing properties of coatings is not clear. And the gas sensing mechanism of the composite coatings needs to be further studied. It is well known that TiO$_2$ is a kind of semiconductor material with excellent electrical properties. The improvement in the gas sensitivity of semiconductor WO$_3$ caused by the doping of TiO$_2$ has been reported. Yet the existing technologies for doping of TiO$_2$ are extremely complicated, which are not appropriate for industrialized production. In addition, the gas sensing mechanism of the coatings doped by TiO$_2$ has not been clearly recognized. According to above consideration, the WO$_3$ based composite coatings doped with TiO$_2$ were prepared by liquid-phase plasma spraying in this paper, and the gas-sensing mechanism of TiO$_2$–WO$_3$ composite coatings was studied systematically.

2. Experimental materials and methods

2.1. Preparation of sprayed slurry

For slurry preparation, tungsten chloride (WCl$_6$) as a precursor was dissolved in the solvent (mixture of distilled water and ethanol with the ratio of 1:1). Then an appropriate amount of nano-TiO$_2$ (particle size 5–10 nm) was added to the solution. The ammonia water was also added to the slurry in order to adjust the pH. The mechanical stirring and ultrasonic vibration methods were used to keep the slurry uniform and stable. During the coating deposition, the slurry was delivered into an atomizer by peristaltic pump. Compressed air of 0.3 MPa was used as the atomizing gas. Thus the slurry was injected into the plasma flame in the form of tiny droplets, and the WO$_3$ solid crystals were formed after heating and evaporating. The purity of all the chemical reagents used in this paper reached to AR grade. The WCl$_6$, NH$_3$·H$_2$O and TiO$_2$ were bought from Aladdin Reagent Co. Ltd. And the C$_2$H$_2$O, C$_2$H$_6$O, HO(C$_2$H$_4$O)$_3$H and H$_2$O were bought from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of gas-sensitive coatings

The substrates used for preparing the gas-sensitive coatings were divided into three layers, where in the bottom layer was a Pt heater, the middle layer was an Al$_2$O$_3$ ceramic plate, and the top layer was Au interdigital electrode (as shown in Fig. 1a). The substrates were cleaned by ultrasonic and air dried. Then the substrates were firstly fixed on a stainless steel plate, and the lower portion of Au electrodes was covered by a mask plate. The WO$_3$ based composite coating was then deposited on the upper portion of Au interdigital electrode via plasma spraying by using the slurry as a feedstock (Fig. 1b). The coating deposition was made by APS-2000K plasma spray system (AVIC Beijing Aeronautical Manufacturing Technology Research Institute, China). The spray parameters used in this research were listed in Table 1. For comparison purpose, the pure WO$_3$ coating was prepared under the same conditions.

2.3. Characterization of microstructure and properties of coatings

The microstructure of the pure WO$_3$ and TiO$_2$–WO$_3$ composite coatings was observed using a field emission scanning electron microscope (FESEM, Hitachi S-550N, Japan) equipped with
a detector of secondary electrons and an energy dispersive spectrometer (EDS). The morphology, sizes and bonding state of the grains in coatings were characterized by transmission electron microscope (TEM, FEI Tecnai F20, Netherlands). X-ray diffraction (XRD, Bruker AXS, Netherlands) and Raman spectrometer (RS, Renishaw in Via Reflex, Britain) were employed to detect the crystal structure and valence of the material in the coatings. The performance of the prepared gas-sensitive coatings was measured. Before testing, the gas-sensitive coating was aged at 200°C for at least three days in order to increase its stability. The sensitivity of the coating was calculated according to Eq. (1) [23]:

$$ S = \frac{R_g}{R_a} $$  \hspace{1cm} (1)

where $R_g$ was the resistance of sensor texted in the measurement atmosphere and $R_a$ was that of sensor texted in the air.

3. Results and discussion

3.1. Effect of plasma power on coatings

A model illustrating the change of the precursor (WCl$_4$) during plasma spraying was schematically depicted (Fig. 1c). It was clear that the formation of coating including several steps as follow: breakdown and refining of droplets → evaporation → concentration → nucleation → growth → formation of solid particles → melted of solid particles → formation of coating. It was well known that the liquid-phase plasma spraying parameters played an important role in each of the steps. And the microstructure of the coatings would be significantly influenced by these parameters.

The effects of the plasma power on the crystallinity and morphology of the coatings were investigated. Fig. 2 showed the XRD and Raman spectra of WO$_3$ coatings prepared under different plasma powers. It could be seen that there were no WO$_3$ peaks in the XRD of the coating deposited at a plasma power of 20 kW. When the plasma power reached 30 kW, the WO$_3$ peaks of the coating became obvious. With the increase of the plasma power (from 30 kW to 36 kW), the WO$_3$ peaks of the coatings were more and more sharp, which indicated that the crystallinity of the coatings increased. The XRD also displayed that the monoclinic WO$_3$ were predominant in all of the coatings prepared by liquid-phase plasma spraying (Fig. 2a). At the same time, the Raman result showed that there were four wavenumber peaks, which were located at 273 cm$^{-1}$, 328 cm$^{-1}$, 715 cm$^{-1}$ and 807 cm$^{-1}$, referring to the monoclinic WO$_3$ in the prepared coatings (Fig. 2b). And it was kept in line with the result of XRD.

The surface morphology of the WO$_3$ coatings prepared under different plasma powers (30 kW, 33 kW, and 36 kW) were also shown in Fig. 2. It can be seen that all of the WO$_3$ coatings presented a loose and porous structure, which was beneficial to the gas sensitivity of coatings (Fig. 2c-e). And as the plasma power raise up to 36 kW, the WO$_3$ had grown larger due to the higher heat input during plasma spraying (Fig. 2e). It was well-known that the larger grains may lead to a lower gas sensitivity of the coatings. Therefore, the plasma power used for the following preparation of WO$_3$ based coatings was fixed to 33 kW in this paper. The morphology of the cross-section in all the coatings obtained in this research was almost the same as that of the surface. And the thickness of the pure WO$_3$ coating...
3.2. Microstructure of TiO$_2$–WO$_3$ composite coatings

A series of TiO$_2$–WO$_3$ composite coatings doped with different amount of TiO$_2$ were prepared, and the pure WO$_3$ coating was fabricated under the same plasma power (33 kW) for comparison. The thickness of the composite coatings was about 5 μm and the porosity was about 8%. The XRD patterns of these composite coatings and pure WO$_3$ coating were shown in Fig. 3a. It could be seen that the peaks in TiO$_2$–WO$_3$ composite coatings were obviously wider than that in the pure WO$_3$ coating, indicating that the particle sizes of the composite coatings were relatively small. There were only WO$_3$ and TiO$_2$ without any new phases in all the composite coatings. It could be concluded that no combination reactions between the WO$_3$ and TiO$_2$ occurred. When the mass ratio of MTiO$_2$:MWCl$_6$ reached 10:100 in the composite coating, the TiO$_2$ peaks appeared in the XRD. In order to further characterize the presentation state of TiO$_2$ and WO$_3$ in the composite coatings, the Raman spectroscopy test was carried out (Fig. 3b). It could be seen that the peaks of both the monoclinic WO$_3$ and anatase TiO$_2$ began to appear with the mass ratio of MTiO$_2$:MWCl$_6$ grew up to 10:100 in the composite coating. When the amount of TiO$_2$ doped in coatings was lower, the peaks of TiO$_2$ disappeared. It was probably due to that the quantity of TiO$_2$ was too little and they were uniformly dispersed. The result of Raman spectroscopy was also kept in line with the XRD (Fig. 3).

The Debye–Scherrer formula was also used to calculate the average grain size of the particles in the composite coatings. The results were shown in Table 2. It could be seen that the average grain size of the composite coating decreased with the increase of TiO$_2$. While the mass ratio of MTiO$_2$:MWCl$_6$ grew up to 20:100, the average grain size of the composite coating became larger. The smallest average grain size was 10.64 nm, which was achieved at a mass ratio of MTiO$_2$:MWCl$_6$ was 10:100. It was reported that the smaller grain size may lead to a larger specific surface area, which was beneficial to the gas sensing performance of the coatings. Thus more attention
would be paid to the TiO₂–WO₃ coating with the mass ratio of MTiO₂:MWCl₆ was 10:100.

The surface morphology and element distribution of the composite coating (MTiO₂:MWCl₆ = 10:100) were tested by EDS (Fig. 4). It can be seen that the WO₃ was evenly distributed around TiO₂ in this coating, and there was a boundary layer between WO₃ and TiO₂ (Fig. 4a–d), which would suggest the generation of semiconductor heterojunctions.

In order to illustrate the microstructure of coatings more intuitively, the transmission electron microscopy of a pure WO₃ coating and a TiO₂–WO₃ composite coating (MTiO₂:MWCl₆ = 10:100) were observed [Fig. 4]. It could be seen that the average particle size of the pure WO₃ coating was about 20–30 nm [Fig. 4e], while that of the TiO₂–WO₃ composite coating was about 10–20 nm [Fig. 4f], indicating that the doping of TiO₂ could effectively inhibit the growth of WO₃. From the high resolution of Fig. 4g, it could be found out that there were two kinds of crystals with different brightness in the composite coating. The distance of crystal face in the brighter one was 0.39 nm, which corresponded to that of WO₃ (002) crystal face. The distance of crystal face in the darker one was 0.24 nm, which corresponded to that of TiO₂ (004) crystal face. Furthermore, the WO₃ and TiO₂ crystals in the figure were closely combined. In conclusion, the high-resolution image provided a clear evidence for the presence of WO₃ and TiO₂ semiconductor heterojunctions in the composite coating.

### 3.3. Gas sensing properties of TiO₂–WO₃ coatings

In this paper, two kinds of coatings prepared using a raw material of pure WCl₆ and the mixture of TiO₂ and WO₃ (MTiO₂:MWCl₆ = 10:100), respectively, were the main study object. And the gas sensitivities of them were investigated deeply. In the gas sensitivity test, the gas sensors worked at a temperature of 100 °C, 150 °C and 200 °C, respectively. The response resistance signals of the above mentioned coatings to 100 ppm NO₂ at different temperatures were shown in Fig. 5. It could be seen that the response and recovery time of TiO₂–WO₃ composite coating to 100 ppm NO₂ was shorter than that of pure WO₃ coating at 100 °C, 150 °C and 200 °C (Fig. 5a–c). The sensitivity (S) of the coatings at different temperatures was calculated by Eq. (1), as shown in Fig. 5d. It was observed that the sensitivity of both the TiO₂–WO₃ composite coating and pure WO₃ coating decreased as the temperature raised. Therefore the coatings prepared in this paper might have better sensitivity at a lower temperatures (100 °C). It might lead to a lower energy consumption and be more suitable for the application of industrial. At the same time, it was obviously that the sensitivity of the TiO₂–WO₃ composite coating was better than that of the pure WO₃ coating. Especially at 100 °C, the former was an order of magnitude higher than the latter.

### 3.4. Analysis of the gas sensing mechanism

During the liquid-phase plasma spraying process, the heating and cooling rates of the precursor (WCl₆) was extremely high. And WO₃ was formed in this non-equilibrium reaction. Therefore, this kind of WO₃ was generally a nonstoichiometric compound. There would be a variety of defects on its surface [24]. And a high capacity to attract gas was obtained by the WO₃ prepared using liquid-phase plasma spraying technology [25]. At the same time, there were many bare crystalline surfaces in this type of WO₃ crystal. When the bare crystalline surfaces were exposed in the air, the oxygen molecules would be captured on the surfaces and a lot of electrons would transfer from the surfaces to oxygen molecules [26]. Therefore, on the near surfaces of the WO₃ semiconductor, many positively charged donors were left, which would lead to a formation of the space charge layer on the surfaces [27]. And there would be a contact barrier between the WO₃ grains at last. It was obviously that the electron transfer between WO₃ grains would be limited by the contact barrier (as shown in Fig. 6a). As the height of contact barrier was positively correlated with the oxygen concentration, the higher oxygen concentration, the larger contact barrier between the WO₃ grains, which would lead to a higher resistance of the WO₃ semiconductor. If the WO₃ grains were exposed in a reducing gas, the reducing
gas molecules would react with the oxygen attracted on the bare crystalline surfaces of WO$_3$. And a part of the electrons trapped by the oxygen before might be returned to the WO$_3$, the thicknesses of the space charge layers on the surface of WO$_3$ grains were reduced. The height of the contact barrier between the WO$_3$ grains might also decrease, and the quantity of electrons crossing the contact barrier might increased, which would result in a reduction in resistance of WO$_3$ semiconductor (as shown in Fig. 6b). Furthermore, the oxidizing gas exhibited a high electron affinity. If the WO$_3$ grains were exposed in an oxidizing gas, on the other hand, the oxidizing gas molecules would capture electrons from the oxygen attracted on the bare crystalline surfaces of WO$_3$ [28]. On the other hand, they might directly capture electrons from the WO$_3$. As a result, the height of the contact barrier between the WO$_3$ grains might increase, leading to an increase in resistance of WO$_3$ semiconductor (as shown in Fig. 6c). The schematic of the fundamental cause of the gas-sensing properties obtained by the WO$_3$ coating was shown in Fig. 6. At the same time, the coatings prepared by liquid-phase plasma spraying contained a quantity of tiny WO$_3$ grains (Fig. 4) and presented a loose and porous structure (Fig. 2). The specific surface area of WO$_3$ coating would be rather large, thus a large number of gas adsorption sites were provided in the coating, and the gas-sensing performance of the WO$_3$ coating would be excellent.
Based on the analysis above, it could be seen that the TiO$_2$ and WO$_3$ semiconductors were uniformly distributed in the TiO$_2$–WO$_3$ composite coatings (Fig. 4). Since TiO$_2$ and WO$_3$ were both n-type semiconductors, the close contact between them would lead to the formation of an n–n-type heterojunction at the interface (Fig. 7). The difference of Fermi energy between the TiO$_2$ and WO$_3$ semiconductors might induce a directional migration of the electrons in the n–n-type heterojunction (Fig. 7a) [29,30]. Then an electron depletion layer in TiO$_2$ and an electron accumulation layer in WO$_3$ were formed, and the thermal equilibrium was achieved (Fig. 7b). It was well known that the electron accumulation layer would promote the oxygen adsorption on the surfaces of gas sensitive materials. And the electron depletion layer might lead to a reduction in conductivity of the composite gas sensitive materials [31,32]. Therefore, the height of the contact barrier would be increased. And a larger initial resistance was obtained by the composite gas sensitive materials, which might indirectly improve the gas-sensing properties of composite materials. This was the reason why the TiO$_2$–WO$_3$ composite coating exhibited even more excellent gas-sensing properties than the pure WO$_3$ coating under the same condition (Fig. 5d).

4. Conclusions

In the present study, a series of WO$_3$ based coatings doped with TiO$_2$ were prepared by liquid-phase plasma spraying. The microstructure and properties of TiO$_2$–WO$_3$ composite coatings has been investigated. The main conclusions are as follows:

Fig. 6 – The schematic of the fundamental cause of the gas-sensing properties obtained by the WO$_3$ coating in different atmospheres: (a) in air, (b) in reducing gas and (c) in oxidizing gas.

Fig. 7 – The formation of an n–n-type heterojunction at the interface between TiO$_2$ and WO$_3$ (a) the directional migration of electrons, (b) the formation of an electron depletion layer in TiO$_2$ and an electron accumulation layer in WO$_3$. 
(1) The most suitable plasma power for the preparation of gas sensitive coatings was 33 kW. As the mass ratio of TiO$_2$:MWCNT was 10:100, the TiO$_2$–WO$_3$ composite coating obtained the smallest average grain size (about 10.64 nm). And this composite coating displayed an excellent sensitivity to NO$_2$, especially at a lower temperatures (100 °C), the sensitivity of the composite coating was about 10 times higher than that of the pure WO$_3$ coating.

(2) The TiO$_2$-doping led to a decrease of the average grain size and an increase of the specific surface area in the TiO$_2$–WO$_3$ composite coating. At the same time, an n–n type heterojunction was formed at the interface of TiO$_2$ and WO$_3$.

(3) The electron depletion layer and electron accumulation layer formed by different Fermi energy between the TiO$_2$ and WO$_3$ semiconductors increased the resistance of the composite coating. It can be conclude that TiO$_2$–WO$_3$ composite coating exhibited rather high gas-sensing properties.

Conflicts of interest

The authors declare no conflicts of interest.

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