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Preparation and room temperature methane sensing properties of platinum-decorated vanadium oxide films

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ABSTRACT

Room temperature methane (CH_4) response characteristics of vanadium oxide (VO_x) thin films loaded with platinum (Pt) nanoparticles were investigated for detection of CH_4. The Pt/VO_x thin films have been prepared on sapphire substrate by means of dc-magnetron sputtering of V metal, followed by deposition of Pt nanoparticles, and then rapid thermal annealing (RTA) in O_2 atmosphere from 450 °C to 470 °C. SEM and XRD were used to investigate the morphology and crystal structure of the films. The results showed that irregular rod-shaped particles with size on the average of 100 nanometers and the monoclinic vanadium dioxide (VO_2) were obtained. The property of metal to insulator transition (MIT) was a confirmation of the prepared VO_2. The sensor annealed at 460 °C showed the largest response value which was 18.2 toward methane (CH_4) at room temperature with the concentration of 500 ppm. The optimal operating concentration for CH_4 detection is 1500 ppm.

1. Introduction

CH_4 is a kind of strong absorbed, flammable and explosive substances as a major constituent of mash gas, firedamp and rock gas. It is well known that a small spark can cause violent explosion and do great damage to human beings if the concentration of CH_4 reaches a critical limit (5%–15%). Up to now, there are various semiconductor oxide nanostructured materials used for the detection of CH_4, for instance, including tin oxide [1,2], zinc oxide [3,4] etc. However, these materials sensors operate at high temperature greater than 100 °C to get good response sensitivity toward CH_4, which could cause a series of problems, such as higher power consumption and a reduction in their stability. Therefore, it is of great importance to develop a convenient and applied gas sensor which can be operated at a low temperature for CH_4 detection.

Among extensive research for nanostructure sensitive materials, VO_x has been studied as a new type of gas sensitive materials. The VO_x family consists of more than ten kinds of compounds with vanadium valence from +2 to +5, such as VO, V_2O_3, VO_2 and V_2O_5 etc. In the meantime, the vanadium dioxide (VO_2) and vanadium pentoxide (V_2O_5) cause intensive research interest due to the property of metal to insulator transition. The transition temperature T_C of VO_2 is around 68 °C [5] with a reversible change from monoclinic structure at low temperature to a high-temperature tetragonal rutile structure with a band gap about 0.7 eV [6]. The transition temperature T_C of V_2O_5 is around 250 °C [7]. They have been successfully applied to storage devices [8,9], switching circuit [10,11] and smart windows [12,13]. There are several commonly used methods to synthesize nanostructured thin films, such as sputtering [14–17], chemical vapor deposition [18,19], sol-gel [20] and pulsed laser deposition [21,22]. To the best of our knowledge, there are only few available articles reported VO_x is associated with detection of CH_4. A.K. Prasad's team [23] firstly reported the single VO_2 thin film for detection of CH_4 by sputtering in 2014. Recent efforts have been concentrated on enhancing the sensitivity and decreasing the operating temperature of methane sensor. More contact surface area such as nanorods and nanowire are preferred for improving sensitivity for CH_4. On the other hand, many reports available claimed adding noble metal [24–26] could enhance the response characteristics of gas sensor attributed to a selective promotion of the desired molecule reaction at different adsorbed locations.

In this paper, we have deposited Pt nanoparticles on the nanostructured VO_x thin films for the detection of CH_4 at room temperature. The Pt/VO_x films sensor structures have been successfully prepared using dc magnetron sputtering for the deposition of metal vanadium thin films, adding bit of Pt particles, and then RTA to obtain nanostructured VO_x films with desired composition and morphology.

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2. Experimental

2.1. Preparation

The sapphire substrates need ultrasonic cleaning first with ethanol and acetone consecutively for 15 min for each step. After cleaning, the sapphire substrates are dried in infrared rapid drying equipment for 5 min. A pairs of interdigitated Pt electrodes are deposited on sapphire substrates with the help of shadow mask by sputtering for two minutes [27].

The high purity vanadium thin films are deposited on the cleaned sapphire substrates by a dc facing-target magnetron sputtering system, using a circular vanadium target of 60 mm in diameter supplied by GRIKIN Advanced Materials Co with a purity of 99.95%. The power is set to 75 W. The basic pressure is 4×10^{-4} Pa and the sputtering pressure is 2 Pa in Ar atmosphere with flow of 48 sccm. The substrate is kept at room temperature during film deposition for 35 min.

After deposition, the sensor substrates are mixed up with Pt nanoparticles onto the surface of vanadium thin films via sputtering, where the power is 100W. The sputtering pressure is 5.5×10^{-1} Pa in Ar atmosphere with flow of 24 sccm.

Oxidization of the sputtered vanadium films is carried out in the rapidly thermal annealing furnace (AG610, manufactured by Allwin21 Corp, USA). For comparison, the films of vanadium are rapidly annealed under different temperatures ranged from 450 °C to 470 °C. The heating rate and duration time are set to be 50 °C/s and 270s, respectively. The flow rate of O_2 is 5 slpm. The schematic diagram of the process for preparation of Pt/VO_x sensor can be seen from Fig. 1.

2.2. Characterization

The surface morphology of VO_x nanostructured thin films are investigated by a field emission scanning electron microscopy (FESEM,FEI Nanosem 430, and Hitachi S-4800). X-ray diffraction (XRD, RIGAKU D/MAX 2500 V/PC, Cu Kα radiation) analysis displays the crystallographic structure of the films. Change of square resistance with temperature of vanadium oxide reveals the phase transition, measured by RTS-8 four probe methods with the help of a temperature controller.

2.3. Gas sensing test

The sensing test of the Pt/VO_x films sensors are measured in a in a dynamic flow system consisting of a polymethyl methacrylate (PMMA) test chamber, four small fans to promote gas diffusion, a professional digital multimeter (NUI-T UT70D) and an automatic data acquisition system. The structure diagram of gas sensing test system is showed in Fig. 2.

Two Au-coated copper probes of the digital multimeter (NUI-T UT70D) contacted with the interdigitated electrodes to continuously measure the electrical resistance of sensor [28]. A certain amount of pure CH_4 gas is introduced into test chamber by a micro-injector, and then removing the movable cover of the top container when the resistance maintain a relatively value. The variation of electrical resistance will be stored in computer as excel file format in every second, then further to form the sensitive curve in the Origin 8 software. The gas sensing test of sensor is only researched at room temperature.

In this report, the sensor response is defined as $S = (R_{AIR} - R_{CH4})/R_{CH4} \times 100$ [29], where R_{AIR} is the initial resistance and R_{CH4} is stable resistance after the injection of CH_4. The response time is defined as the time for 90% of the total resistance change. Similarly, the recovery time is the time for 90% of recovery the resistance change.

3. Results and discussion

3.1. Surface morphologies

The top view SEM images demonstrate the influence of annealing temperature and doping Pt nanoparticles on the surface morphology. As shown in Fig. 3(a), the VO_x film without Pt

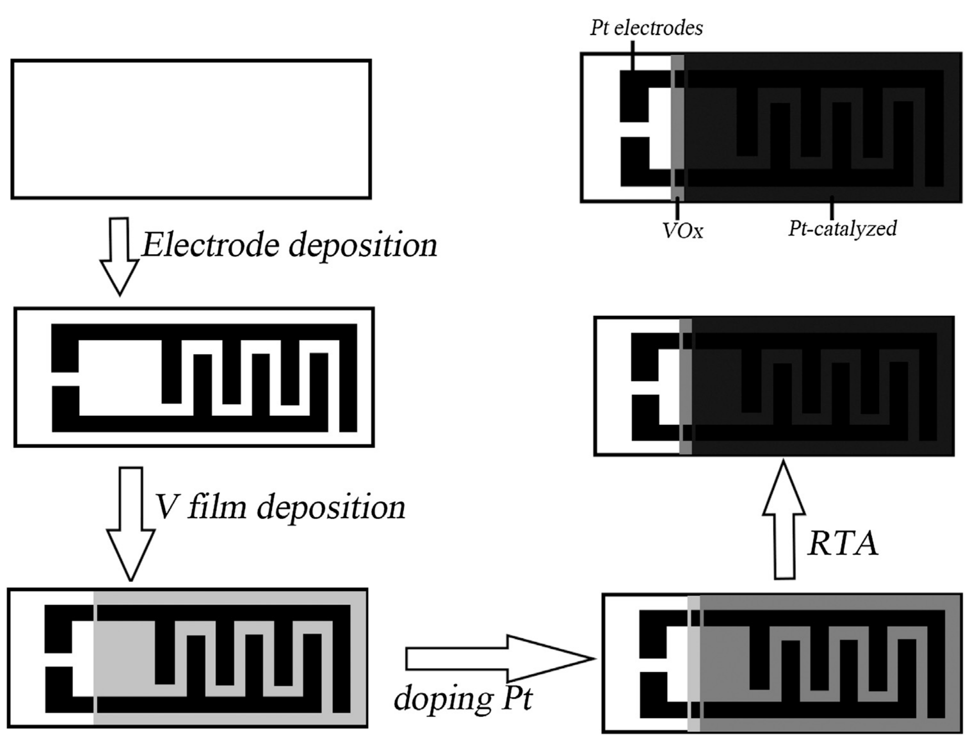

Fig. 1. Schematic diagram of the process for preparation of the Pt-catalyzed VO_x films sensor.