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High hydrogen response of Pd/TiO_2/SiO_2/Si multilayers at room temperature

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ABSTRACT

A series of Pd/TiO_2/SiO_2/Si multilayers were produced using magnetron sputtering method. It is found that H_2 molecules have dramatic effect on the current–voltage (*I–V*) characteristics of the Pd/TiO_2/SiO_2/Si multilayers at room temperature (RT). When Pd/TiO_2/SiO_2/Si multilayer is exposed to H_2, the Pd film quickly reacts with H_2 and forms palladium hydride which results in transferring more electrons from the Pd film to TiO_2 film. Therefore, the *I–V* characteristic of Pd/TiO_2/SiO_2/Si multilayer was greatly changed when exposed to H_2. For example, a Pd/TiO_2/SiO_2/*p*-Si multilayer can show a high response (~2431%) to 1% H_2 with appreciable short response time of 13 s and recovery time of 4 s at RT. Besides, it is demonstrated that Si substrate has a great effect on the H_2 response of Pd/TiO_2/SiO_2/Si multilayers. When exposed to H_2 the current of Pd/TiO_2/SiO_2/*p*-Si multilayer at −0.5 V greatly decreases while the current of Pd/TiO_2/SiO_2/*n*-Si multilayer greatly increase, which can be understood by their energy band structures.

1. Introduction

Hydrogen (H_2) as a kind of new-type and clean fuel has become one of the best choice to replace fossil energy in future. However, H_2 is colorless, odorless, explosive and extremely flammable with lower explosive limit of 4% in air. Consequently, a reliable sensor is needed to detect leakage from the storage and transportation of H_2 as well as to monitor its concentration over a wide range. However, the shortcomings of current H_2 sensors, such as big volume, expensive price, working at high temperature, greatly limit their performance. Therefore, the development of new-type H_2 sensor material possesses extremely important scientific significance [1,2].

The nanometer oxide semiconductor gas sensor with high response, light stability, corrosion resistance and simple measurement has attracted much attention [3]. For example, nano zinc oxide (ZnO) gas sensors, nano tin oxide gas sensors and nano titanium oxide (TiO_2) etc. gas sensors show high response to polar gases [4–6] and can detect gases in harsh environments [7]. Recently, it was found that the TiO_2 nanotubes and nanowires not only can detect the polar gases, but also show certain response to non-polar gases such as H_2, carbon dioxide [8,9]. TiO_2 nanotubes or nanowires arrays sensors show high response (~1000%) to 0.1% H_2 [8,10], its response time and recovery time in H_2 gas can reach to 13 s and 120 s, respectively [11,12]. In addition, it is found that the precious metals such as palladium (Pd) etc. can further improve the sensing performance of TiO_2 nanotubes and nanowires [13–15]. Though gas sensing performance of TiO_2 nanotubes and nanowires is excellent, they possess several shortcomings such as strict preparation, complex processing and high cost, which will make them difficult to realize industrialization. In addition, these gas sensors tend to obtain better gas response at high temperatures [16].

Compared with TiO_2 nanotubes and nanowires, TiO_2 film can be simply prepared using many low-cost methods. Moreover, the electronic structure of TiO_2 thin film can be modulated by compounded with other semiconductor materials [17], doped with nonmetallic element [18,19] or modified by precious metal [20–23]. Recent studies demonstrated that TiO_2 thin film is also sensitive to H_2. For example, TiO_2 film doped with Pd shows fast response time (5 s) in H_2, its gas response in 0.05–0.1% H_2 is more than 40% at 300 °C [23,24]. It is also found that TiO_2 film showed good response (270%) at 200 °C in 0.1% H_2 [25] and response time (1 min) in 1% H_2 [26]. In addition, it is demonstrated that TiO_2 film sensor shows response (~55%) to H_2 with a short response time (2 s) at 175 °C in 1% H_2

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with N_2 as carrier gas [27]. In a word, compared with TiO_2 nanotubes and nanowires the gas response of TiO_2 film is very low. How to further improve the gas response of TiO_2 film?

Recently, it is found that the interfacial effect of the heterojunction is similar to an excellent "amplifier" and at room temperature (RT) can make the gas response of amorphous carbon film increase more than 2–5 orders of magnitude [28–32]. Based on the above discussion, we put forward an idea to improve the H_2 gas response of TiO_2 film. Herein, we use the interfacial amplification effect of TiO_2 film/SiO_2/Si heterojunction to enhance the H_2 sensing properties of TiO_2 film. It is found that a Pd/TiO_2/SiO_2/*p*-Si multilayer can show a high response (~2431%) to 1% H_2 with appreciable short response time of 13 s and recovery time of 4 s at RT. In other words, the gas response and response time of Pd/TiO_2/SiO_2/Si heterojunction are comparable to that of TiO_2 nanotubes array.

2. Materials and experiments

2.1. Synthesis and characterization of Pd/TiO_2/SiO_2/Si structure

The fabrication of Pd/TiO_2/SiO_2/Si sensors can be briefly described as follows: first, a TiO_2 film was grown on Si ⟨1 0 0⟩ substrate (10 mm × 10 mm) with native oxide layer (1.2 nm) [33] using RF magnetron sputtering method. The resistivities of *p*-Si or *n*-Si substrates (the 46 Institute of Ministry of Electronics Industry, Tianjin, China) are 0.1–1 Ω cm and 1–10 Ω cm, respectively. The Si substrates were successively cleaned in ethanol and acetone solution using ultrasonic (Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China) for 5 min, in the cleaning process no etching solution was used. TiO_2 target is purchased at Beijing Jinyan Zhong new material Co., Ltd., Beijing, China. Before depositing TiO_2 film, the sputtering chamber was pumped below 2×10^{-4} Pa and Si substrate was kept at RT. The working gas during deposition was mixed gas of argon and oxygen, two kinds of gas proportion is 1:1. The total gas pressure is 5 Pa, both oxygen and argon partial pressures are 2.5 Pa. In the deposition process, gas pressure, deposition power and time were 5 Pa, 90 W and 90 s, respectively.

Second, the Pd film was deposited on the TiO_2/SiO_2/Si structure utilizing a metal mask from a Pd target (Beijing Mountain Technical Development Center, Beijing, China) using DC magnetron sputtering. In the deposition process, argon gas pressure, deposition power and time were 3 Pa, 40 W and 2 min, respectively. The substrate was still kept at RT. Thus the Pd/TiO_2/SiO_2/Si was prepared and its structure is illustrated in Fig. 1. The size of Pd film is 5.0 mm × 5.0 mm. The Pd film was used as sensitive layer. Moreover, it should be noted that the electrodes on the Pd film and Si substrate were made by In solder. Ohmic contact can be formed between In and Pd film or In and Si substrate. The interface barriers are very little or no contact barrier even, which have little influence on *I–V* characteristics of the Pd/TiO_2/SiO_2/Si junction. The thicknesses of the TiO_2 film and Pd film are about 15 nm and 16 nm, respectively, which are measured using Scanning Electron Microscopy. Finally, the crystal phases was observed with X-ray diffraction (XRD) on X'Pert Pro MPD XRD system (Cu*K*α1, λ = 1.5406 Å). It is demonstrated that the TiO_2 thin film is amorphous.

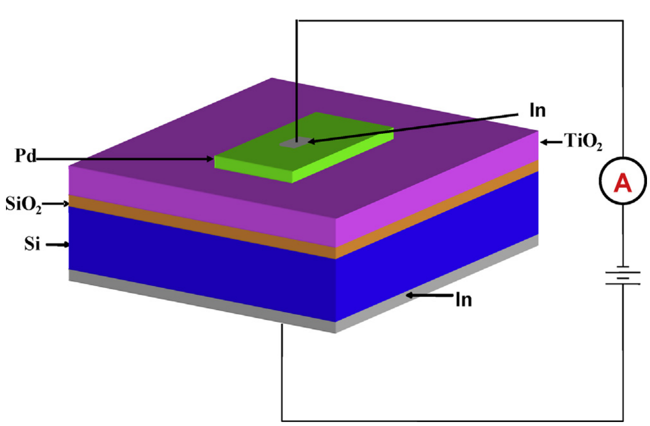

Fig. 1. The schematic illustrations of the *I–V* measurement of Pd/TiO_2/SiO_2/Si multilayers.

2.2. Hydrogen sensing measurement

All the H_2 sensing measurements were conducted in a chamber by exposing the multilayers to different concentrations of H_2 (Qingdao Tianyuan Gas Production Limited Company, Qingdao, China) in air at RT (24 ± 1 °C). The relative humidity in air is 30% and the air pressure is 1.0×10^5 Pa (normal pressure). The *I–V* characteristics of Pd/TiO_2/SiO_2/Si multilayers were measured using two-probe method. The two electrodes of each sensor were mounted on a probe holder and connected to Keithley 2400 source-meter (Keithley Instruments Inc., Cleveland, U.S.) controlled by a computer.

3. Results and discussions

3.1. I–V characteristics of Pd/TiO_2/SiO_2/Si multilayers

Fig. 2a shows the *I–V* curves of the as-fabricated Pd/TiO_2/SiO_2/*p*-Si (In contact on *p*-Si is anode) and Pd/TiO_2/SiO_2/*n*-Si (In contact on *n*-Si is cathode) multilayers in air and pure H_2 at RT. The *I–V* curve of the Pd/TiO_2/SiO_2/*p*-Si multilayer in air shows that Pd/TiO_2/SiO_2/*p*-Si is conductive when it is loaded positive or

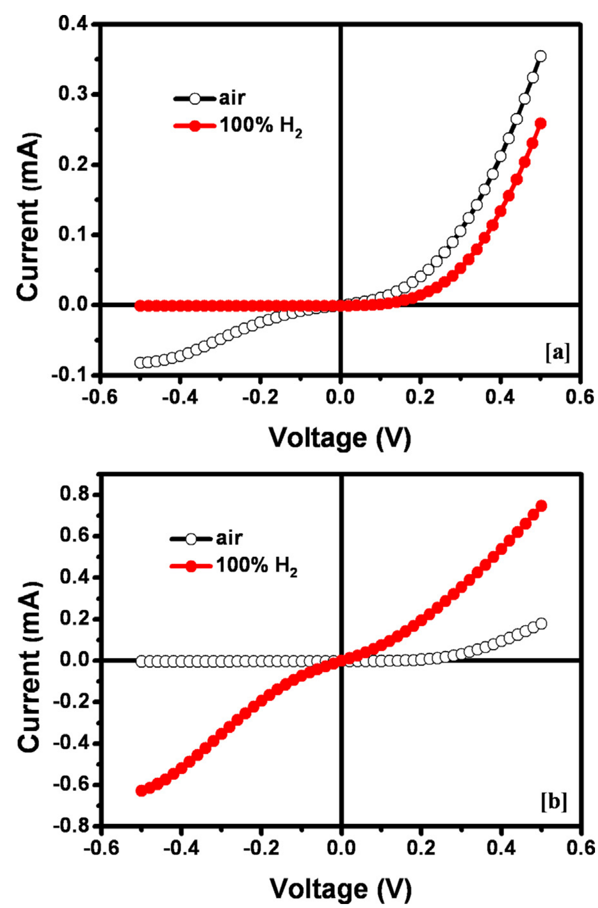

Fig. 2. Plots of measured *I–V* curves of (a) the Pd/TiO_2/SiO_2/*p*-Si and (b) Pd/TiO_2/SiO_2/*n*-Si multilayers in air and after exposure to pure H_2 at RT.