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Thermoelectric hydrogen sensor working at room temperature prepared by bismuth–telluride P–N couples and Pt/γ-Al_2O_3

Hu Huang, Weiling Luan*, Jian-Song Zhang, Yun-Shi Qi, Shan-Tung Tu

School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai 200237, PR China

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Abstract

A hydrogen sensor working at room temperature with high sensitivity, good selectivity and simple structure was presented in this paper. Four couples of P- and N-type bismuth–telluride films were connected in series to serve as the feedback part of the hydrogen sensor with a high Seebeck coefficient of 1.1 mV/K. A platinum catalyst was deposited on γ-Al_2O_3 acting as a sensitive part. Linear relationships between the output voltage and the hydrogen concentration as well as the flow rate were found when the hydrogen concentration was higher than 0.5 vol.%. As for the 3 vol.% H_2/Air gas with a 100 ml/min flow rate at room temperature, the response and recovery times were about 30 and 55 s, respectively, and the error of repeatability was less than 0.3%.

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1. Introduction

Thermoelectric (TE) materials have been widely used in clean energy systems as a low-power generator and a Peltier cooler, due to its salient features of being compact, light-weighted, noiseless in operation, highly reliable, and environment friendly. Besides, TE materials have been explored to prepare gas sensors based on Seebeck effect and exothermic reaction.

In this paper, a TE-hydrogen sensor was investigated. Two functional parts, TE films and a catalyst, compose the core of a TE-hydrogen sensor. The catalyst accelerates the exothermic oxidation of hydrogen to quickly generate heat on one part of the TE films, and then a temperature difference was built up along the two sides of the TE films. Then the TE films, working as a feedback part, convert the temperature difference into a voltage as an output signal. The innovative idea of the TE-hydrogen sensor was first introduced by McAleer et al. [1] in 1985, and their sensor was prepared via sputtering platinum onto a flat surface of a porous tin-dioxide pellet. During the operation, platinum and tin-dioxide were employed as the catalyst-sensitive part and the TE-feedback part, respectively. However, the sensitivity of this sensor was limited because of its low-output voltage. Shin et al. [2–5] took Li–NiO or B–Si–Ge as a feedback part and used a Pt-film or Pt/α-Al_2O_3 as a catalyst to fabricate better TE-hydrogen sensors, and modified the substrate by plasma enhanced chemical vapor deposition (PECVD) and etching technologies to reduce its thermal conductivity for keeping the temperature difference on the TE materials. Especially, a sinuate Pt-belt was deposited as a film heater to satisfy the high temperature working condition requirement.

In our research, two methods have been extended to improve the sensitivity of the TE-hydrogen sensor: one is to create a larger temperature difference via an effective catalyst to generate more heat; the other way is to increase the Seebeck coefficient of the TE part by structure design. Here bismuth–telluride P–N couples and a Pt/γ-Al_2O_3 catalyst were chosen as the feedback and sensitive parts. The design of the P–N couples, properties of the catalyst, and relationships between the output voltage and the hydrogen concentration as well as the flow rate were studied.

2. Experimental

2.1. P–N couples fabrication

Bismuth–telluride was chosen as the feedback part operating without an extra heating supplier due to its high performance at

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* Corresponding author.
E-mail address: luan@ecust.edu.cn (W. Luan).

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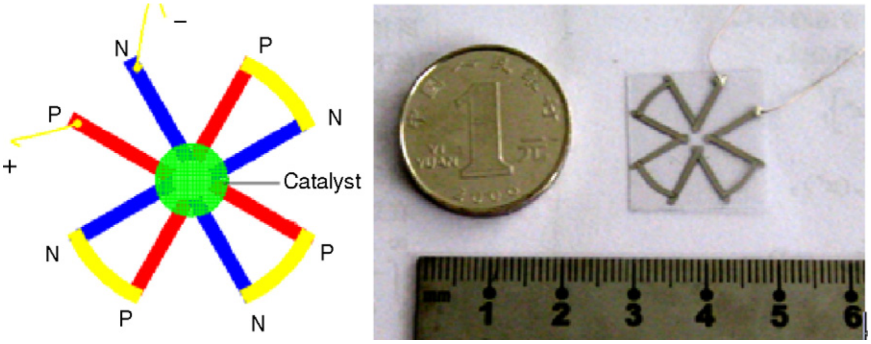

Fig. 1. The sketching (left) and practical (right) pictures of PN-4 junction.

room temperature. Here P- and N-type films were deposited on a glass substrate (20 mm × 20 mm × 0.2 mm) via rf magnetron sputtering with mixed powder targets, where the molar ratio of Bi:Sb:Te for P-type was 1:3:6 and Bi:Te for N-type was 1:1. Four pairs of P- and N-legs (marked as PN-4) were deposited with a shape of 8 mm × 1 mm through a pre-designed steel mask. The TE legs were arrayed centrally symmetric and then connected in series in order to enhance the total Seebeck coefficient. Heat treatment was not carried out to these deposited TE films, considering that the Seebeck coefficient would be reduced after annealing. The sketch and practical picture of the PN-4 junction are shown in Fig. 1.

2.2. Catalyst preparation

Due to its high specific surface area, γ-Al_2O_3 was chosen as the support for a Pt-catalyst. Catalyst paste was prepared by stirring the mixture of γ-Al_2O_3 powder and an aqueous solution of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), and then dropped onto a PVC mold, which was shaped with dozens of uniform cavities with diameter of 4 mm. As-shaped drops were exposed in air for several hours, and then dried between 70 and 100 °C, in order to prevent the crack formation from the quick evaporation of water or removing of chloride ions. The Pt loading could be further improved by impregnation of the as-dried catalyst with the $H_2PtCl_6{\cdot}6H_2O$ solution, and 10 wt% of Pt-load was adopted. After calcined at 400 °C for 2 h, a reduction process was conducted at 200 °C for 2 h under pure hydrogen atmosphere with a flow rate of 50 ml/min. The as-treated Pt/γ-Al_2O_3 catalyst was fixed at the center of PN-4 with heat conductive glue (Dow corning 3140 Adhesive/Sealant) to ensure the heat being transferred steadily to all couple joints.

2.3. Properties observation and measurements

The crystal structures of the TE films were investigated by X-ray diffraction (XRD, Rigaku D/max 2550, Japan), and the Seebeck coefficient of PN-4 was measured with a constant temperature difference method. The surface morphology of the Pt/γ-Al_2O_3 catalyst was observed with field emission-transmission electron microscope (FE-TEM, JEOL JEM-2100F, Japan). 3 vol.% H_2/Air, CH_4/Air and CO/Air were tested for the selectivity of the catalyst, considering the 60% of current H_2 was produced via a methane steam reforming method, where CH_4 and CO were inevitably shown up as the reactant and a side-product. The as-combined sensor was placed in an airproof chamber, testing gases and pure nitrogen were alternatively blown through the surface of the catalyst, and the flow rate was concisely adjusted by a gas flowmeter. The voltage and the temperature were measured by a nano-voltmeter (Keithley 2182, USA) and R-type thermocouples with a diameter of 0.07 mm, respectively. All data were collected by a data acquisition/switch unit (Agilent 34970A, USA).

3. Results and discussion

3.1. Crystal structure and Seebeck coefficient of TE couples

Fig. 2 shows the XRD patterns of the P- and N-type films deposited by rf magnetron sputtering, because of its higher vapor pressure, Te is easier to be deposited onto a substrate, comparing with Bi in the same target, resulting in a composition deviation between the film and the target. The XRD analysis revealed that an extra Te phase remained both in P- and N-type films, and the Te phase was even reported to be helpful in enhancing the Seebeck coefficient of P-type films [6]. On the other hand, N-type films were found with a predominant composition of the Bi_2Te_3 phase due to the previous addition of more Bi in the sputtering target.

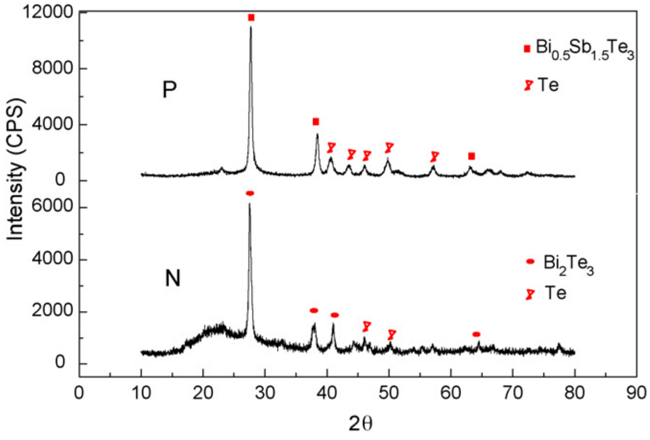

Fig. 2. XRD of P- and N-type films sputtered with $Bi_{0.5}Sb_{1.5}Te_3$ and Bi_2Te_3 powder targets, respectively.

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