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Sputtered platinum thin films for resistive hydrogen sensor application

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ABSTRACT

This work presents hydrogen (H_2) sensing properties of platinum (Pt) thin film deposited on glass substrate by sputter technique. The Pt thin films with different thickness prepared using RF sputtering method were characterized by the XRD, SEM and XPS techniques. Temperature dependent resistances and the gas measurements of the Pt thin films were investigated under a dry air flow at a temperature range from 30 °C to 200 °C. The H_2 sensing properties of Pt thin film sensors were also examined in the concentration range of 0.1–1% H_2. The results revealed that the Pt thin film with 2 nm thickness exhibited the best sensing performance to H_2 at 30 °C under dry air flow.

1. Introduction

The detection of H_2 in a wide range concentration is crucial for leak detection, safety issue and real time quantitative analysis [1–4]. Various types of H_2 sensors have been extensively studied depending on physico-chemical detection mechanism such as catalytic, electrochemical, resistor based, work function based, mechanical, optical and acoustic. The resistor based hydrogen sensor could be divided into two parts as metallic resistor and semiconducting metal oxide resistor sensors. In general, palladium (Pd) and Pd alloy are used as sensitive materials for metallic resistor type hydrogen sensor [1–4]. Apart from Pd and Pd alloy, there are a few numbers of publications about Pt resistive H_2 sensor. Different types of Pt nanostructures such as thin film [5–7], nanoporous film [8,9] and nanowire [10,11] were fabricated for H_2 sensor applications. All of these studies show that H_2 sensing performance and mechanism of Pt nanostructures are needed much more effort to well understand. This study devoted that, Pt thin films were sputtered on the glass substrates and their H_2 sensing properties were investigated depending on film thickness, temperature and concentration.

2. Experimental

The Pt thin films (2–50 nm) were prepared using RF sputtering method on a glass slide. The films were coated with a constant RF power 50 W at 5 m Torr argon pressure during deposition by using a NONOVAK 400 PVD system. The structural characterizations of the films were studied by Scanning Electron Microscopy (SEM, ZEISS EVO LS15), X-ray diffraction (XRD, Rigaku Smartlab diffractometer), and X-ray photoelectron spectrometer (XPS, Thermo 10 Scientific K-Alpha with monochromatic Al Kα radiation (1486.3 eV)).

Four Au pad electrodes were contacted on the top of Pt thin films for H_2 gas sensing measurements. The changes of resistance for each film were recorded via a four point-probe connected to a multimeter (Agilent 34410 A). The concentrations of H_2 in high purity dry air were varied from 0.1–5%. Resistance-time characteristics of the sensors were measured by changing atmospheric conditions from 30 to 200 °C. The percentage sensitivity %, where $\mathbf{R_g}$ is the resistance exposed to the H_2 and $\mathbf{R_0}$ is the baseline resistance under dry air, defined as:

$$\mathbf{S} = \frac{\mathbf{R_0} - \mathbf{R_g}}{\mathbf{R_g}} \boldsymbol{x} 100 \quad (1)$$

3. Results and discussions

SEM images, XRD and XPS patterns of Pt thin films are displayed in Fig. 1. All films are quite smooth and homogeneously covered on the glass surface. In Fig. 1d, the patterns show strong (111) and (200), and weak (200) and (131) reflections, which correspond to a face-centered cubic crystalline structure [12–13].

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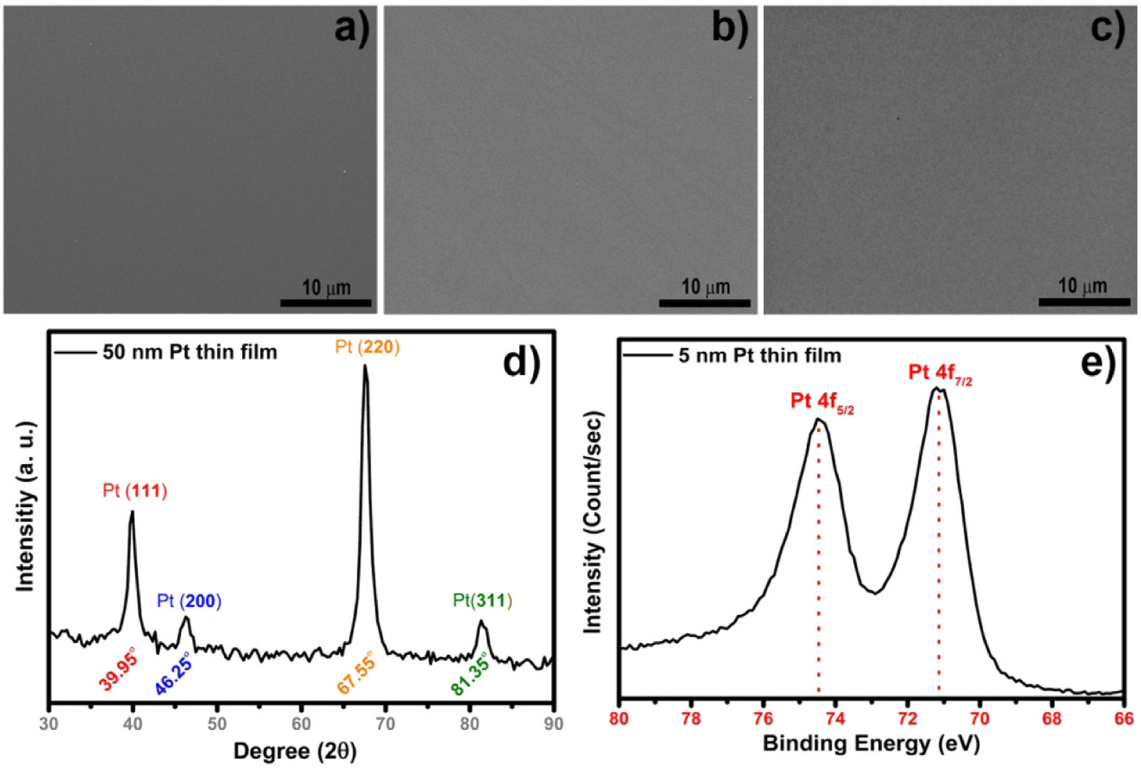

Fig. 1. SEM images of Pt thin films with the thickness of (a) 2 nm, (b) 5 nm, (c) 15 nm. XRD patterns for 50 nm Pt thin film (d) and XPS spectra of Pt4f for 5 nm Pt thin film (e).

Fig. 1e shows that the peaks positions of Pt $4f_{7/2}$ and $4f_{5/2}$ were about 71.1 eV and 74.5 eV correspond to pure Pt metallic state [14].

The resistance-time graph of the 2 nm and 5 nm Pt thin film sensors under 1000 ppm H_2 at the indicated temperatures is given in Fig. 2a–b. After exposure to 1000 ppm H_2, the resistance of both the sensors decreased and then, the rate of decline reached saturation for all measured temperatures. During recovery with dry air, the resistance of the sensors increased rapidly and then come to saturation. The base line of both the sensors are shifted at 30 °C and 100 °C. But, both the sensors are fully reversible above 100 °C. The base line resistances of the sensors increased by enhancing the temperature due to the its metallic structure. Previously, Patel et al. investigated the structure and H_2 response of the Pt film depending on temperature and H_2 concentration [7]. They reported that exposure to ppm level of H_2 in the presence of 5% oxygen with nitrogen as the carrier gas caused decreases in electrical resistance and the sensitivity of the film became more pronounced with increasing temperature. Yang et al. reported the performance of a single Pt nanowire for detecting H_2 in air comparison with Pd nanowire [10]. Yoo et. al investigated H_2 gas sensing properties of the Pt nanowires and explained the sensing mechanism with reduced electron scattering in the cross section of the hydrogen adsorbed Pt nanowires [11].

In our case, the sensing mechanism of Pt thin films could be explained as follow; Pt does not form a bulk hydride phase upon exposure to H_2 such as Pd [7,10,11]. Hydrogen sensing mechanism is schematically given in Fig. 2c. The Pt surface covered with the absorbed oxygen atoms under dry air (Fig. 2c–1). Hydrogen atoms start to displace oxygen on the Pt surface during hydrogen exposing (Fig. 2c–3). After whole surface of the film covered with hydrogen, the number of charge carrier scattering at the Pt surface decreases. So, the decrease in the film resistance exposed to hydrogen could be related to decreasing the number of the surface charge carrier scattering. The ad/absorption and desorption of hydrogen and oxygen in dry air from the film surface could be explained with some reactions [15–16]. When the molecular oxygen reacts with Pt surface in dry air, chemisorbed oxygen atoms form. If the atmosphere changes from dry air to molecular hydrogen, hydrogen atoms displace oxygen atoms on the Pt surface with catalytic formation of water and its desorption from the Pt surface. While the chemisorbed hydrogen atoms on Pt surface react with dry air condition, oxygen atoms replace hydrogen atoms on the Pt surface with water formation. The replacement of the surface atoms (hydrogen or oxygen) is a reversible process.

Temperature dependent sensitivities for 2 nm and 5 nm Pt thin film sensors against 1000 ppm H_2 were given in Fig. 3a. The sensitivites of 2 nm and 5 nm Pt thin film sensors decreased from 2.7 and 0.7–1.1 and 0.3 with increasing temperature, respectively. The sensitivities of 2 nm Pt thin film sensor is higher than the sensitivities of 5 nm Pt thin film sensor for the measured temperature interval. So, the sensitivities of Pt thin films for H_2 is strongly affected by the thickness of Pt film. Similarly, this behavior has been observed for Pt nanowire with different dimensions [10,11]. The response time (t_{90}) is defined as the times required for the change in the resistance variation level of 90% upon initiating the desired H_2 concentration. Fig. 3b shows the response time as a function of temperature for both 2 nm and 5 nm Pt thin film sensors. The response time of 2 nm Pt thin film sensors is lower than that of 5 nm Pt thin film sensor at room temperature and this behavior could be explained with a short diffusion path. But above the temperature of 100 °C the response time of the both sensors is approximately the same as shown in Fig. 3b. The response time is also decreased with increasing temperature for the both sensors and this behavior can be explained with a faster diffusion of hydrogen at higher temperatures.

To investigate concentration dependent H_2 sensing properties, a measurement was performed at 150 °C for 2 nm Pt film sensor due to fully reversible and recovery properties that observed for