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Sol–gel synthesized Titania nanoparticles deposited on porous polycrystalline silicon: Improved carbon dioxide sensor properties

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ABSTRACT

Titania nanoparticles (TNPs) were synthesized by a sol–gel method in our laboratory using titanium tetrachloride as the precursor and isopropanol as the solvent. The particles' size distribution histogram was determined using ImageJ software and the size of TNPs was obtained in the range of 7.5–10.5 nm. The nanoparticle with the average size of 8.5 nm was calculated using Scherrer's formula. Homogeneous and spherical nanoparticles were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and UV–visible spectroscopy (UV–vis). The X-ray powder diffraction analysis showed that the prepared sample (TNPs) has pure anatase phase. TNPs were deposited on porous polycrystalline silicon (PPS) substrate by electron beam evaporation. The TNPs thickness was 23 ± 2 nm at 10^{-5} mbar pressure at room temperature. Porosity was performed by an anodization method. Since polycrystalline silicon wafers consist of different grains with different orientations, the pore size distribution in porous layer is non-uniform [1]. Therefore, the average diameter of pores can be reported in PPS layer analysis. Average diameter of pores was estimated in the range of 5 μm which was characterized by FESEM. The nanostructured thin films devices (Al/Si/PPS/TNPs/Al and Al/Si/PPS/Al) were fabricated in the sandwich form by aluminum (Al) electrodes which were also deposited by electron beam evaporation. Electrical measurements (I–V curves) demonstrated the semiconducting behavior of thin film devices. The gas sensitivity was studied on exposure to 10% CO_2 gas. As a result, conductivity of devices increased on exposure to CO_2 gas. The device with TNPs thin film (Al/Si/PPS/TNPs/Al) was more sensitive and, had better response and reversibility in comparison with the device without TNPs thin film (Al/Si/PPS/Al).

1. Introduction

Metal-oxide semiconductors are widely used for detecting small amount of target gas in air that changes the electrical resistance [2–8]. Titanium dioxide (TiO_2 or Titania) is one of the most prevalent oxide materials for its superior characteristics on different fields like photoelectrochemistry. Titania nanostructures are especially important because they often improve the photocatalytic function and have properties different from bulk counterparts [9]. Titania nanoparticle is also used for important applications such as high refractive index, non-toxicity and chemical inertia in acid solution. Therefore, it has many

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possible utilizations in photocatalysis, polymer industry, white pigment [10], gas sensitivity and corrosion protection coating [11]. Titania nanoparticles can be prepared by different methods like electrical arc discharge, microemulsion, chemical bath, sol–gel, etc. Titania exists in three phases—rutile, anatase and brookite. The rutile and anatase phases both have a tetragonal crystalline structure and can be obtained by heating the amorphous phase at different temperatures [12], and brookite has an orthorhombic structure.

The rutile is thermodynamically the most stable Titania phase [13]. The anatase and rutile phases usually have industrial utilizations. The anatase is also a useful catalyst in photochemistry because of its high photoactivity. The rutile is a common white pigment used for its superior optical hiding power [12]. The properties of surface are distinguished for nanosized oxide powders where the ratio of surface/volume is much more than the ratio in bulk materials; the previous one is especially important for gas sensing utilizations [14]. In automobile industry, much effort has been made to measure exhaust and toxic gases such as CO_X or NO_X. Li et al. have compared different phases of Titania films. The anatase Titania nanoparticles showed an n-type reaction against CO_2 [15].

Porous silicon (PS) has recently been discussed as a novel material for chemical sensors and biosensors [16–18] and its high reactivity and utilizations on large specific surface areas [19,20]. The pore size in the electrochemically synthesized PS can easily be adjusted in nanometers to several micrometers by choosing appropriate etching conditions [21,22]. One method of embedding pores in silicon is performed with the use of an anodization cell; possible anodization cell uses platinum cathode and silicon wafer anode immersed in Hydrogen Fluoride (HF) diluted in ethanol (C_2H_5OH). The anode is corroded by running electrical current in the cell.

Many methods have been used in fabrication of metal-oxide semiconductor sensors. Most important factors include; low-cost (there are restrictions in using expensive films), purity, porosity (if the material is highly porous, the surface area exposed to the gas for interaction will be far higher, giving a higher sensitivity), reliability and reproducibility [21,22]. A study conducted by Rocchia et al. showed that the possibility of chemical change on the surface of PS, obtaining an amine terminated surface, and then used as a sensing element for carbon dioxide detection [23].

In this research, TNPs were synthesized by a sol–gel method which is particularly suitable for homogeneous size distribution. Then, TNPs were deposited on PPS as a substrate by electron beam gun evaporation. Aluminum electrodes were also deposited by an electron beam evaporation method and the nanostructure thin films and sandwich devices (Al/Si/PPS/TNPs/Al and Al/Si/PPS/Al) were fabricated. In this paper, the optical band gap and electrical properties of TNPs/PPS bilayer films were calculated at different temperatures and devices were used as a CO_2 gas sensor. The change of electrical resistance is measured as the output, if a particular vapor is adsorbed by the film and affected the resistance, so a simple ohmmeter or electrometer is enough to collect the data. The response and recovery times, and reversibility of devices were also investigated for carbon dioxide gas sensing.

2. Experimental section

2.1. Synthesis and characterization of TNPs

Titanium tetrachloride (Merck-7550-45-0) and isopropanol (Merck-67-63-0) were used as precursor materials for the synthesis of TNPs by the sol–gel method. The synthesis process was fulfilled as follows: a solution of titanium tetrachloride and isopropanol in the proportion of 1: 8 respectively was constantly stirred in 500 rpm speed for 30 min at room temperature. The color of solution was light yellow and then it was dried at 100 °C in oven, consequently anatase TNPs were produced by calcination at 450 °C for 2 h. The surface morphology of nanoparticles was investigated using an AFM Park scientific instruments model Auto probe CP and FESEM Philips model XL3 instrument made in Holland. UV–vis analysis (Perkin-Elmer UV–vis spectrometer) was also performed. TNPs were characterized by X-ray diffraction with an Equinox 3000 made by Fa. Inel (France), using CuKα radiation, with an accelerating voltage of 40 kV and output current of 25 mA.

2.2. Preparation and characterization of PPS

Porosity was calculated by an anodization method. The substrate was p-type polycrystalline silicon wafer with resistivity 0.4–2 Ω cm and thickness 330 ± 40 μm. Two Al electrodes were deposited by an electron beam gun with the thickness of 80 ± 2 nm and 40 ± 2 nm and with the pressure of 10^{-5} mbar at room temperature. The deposition rate was controlled at 0.5–1.0 Å/s at room temperature. The electrolyte solution in the anodization process was composed of HF (47%) and C_2H_5OH (99.99%) with the ratio of 1:6, respectively. The constant current density of anodization was 7 mA/cm^2 for 20 min. Al/Si acted as anode and platinum plate acted as cathode. The surface morphology of PPS was observed by FESEM with a Philips model XL3 made in Holland. The average diameter of pores obtained was approximately 5 μm.

2.3. Device fabrication and electrical properties

The produced anatase TNPs as a thin layer with the thickness of 23 ± 2 nm were deposited on Al/Si/PPS layers by the electron beam gun and then Al electrode was deposited on TNPs layer in sandwich form with the thickness of 40 ± 2 nm at room temperature. The (I–V) characterization of Al/Si/PPS/TNPs/Al and Al/Si/PPS/Al devices was measured at different temperatures and the current ratio (I/I_0) of the sensors (Al/Si/PPS/TNPs/Al and Al/Si/PPS/Al) was monitored by continuously recording the currents at constant potential using a stable DC power supply and a digital electrometer (Keithley 61OC). The current–voltage (I–V) measurements were carried out in different voltages at room temperature. The sensitivity of devices against of 10% CO_2 was also estimated in the same voltages.