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Chemical Physics Letter

Elixir Chem. Phys. Letter 48 (2012) 9626-9628

ISSN: 2229-712X

The preparation of TiO_2 nanoparticles and investigation of its electrical properties as CO_2 gas sensor at room temperature

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ARTICLE INFO

Article history:

Received: 7 May 2012;

Received in revised form:

28 June 2012;

Accepted: 26 July 2012;

Keywords

TiO_2 Nanoparticles (TNPs),

Sol-gel method,

Porous poly silicon,

CO_2 gas sensor.

ABSTRACT

TiO_2 Nanoparticles (TNPs) were prepared by sol-gel method using $TiCl_4$ as the precursor and propanol as the solvent. The sizes of TNPs were about 4 nm and were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Visible spectroscopy (UV-vis). The X-ray powder diffraction studying explains that all the prepared samples have pure anatase phase tetragonal system. The gas sensing properties of TNPs were also investigated. We prepared porous poly silicon in nano and micron pores size by chemical electrolysation method and deposited TNPs by vacuum system (electron beam gun) with 23 nm thickness on porous poly silicon by sandwich method. I-V, and C-f curves was plotted. Gas sensing of this sandwich device increased in presence of TNPs in comparing with porous poly silicon without TNPs at room temperature by CO_2 gas.

Introduction

In recently years, Nanotechnology was attracted special attentions in human's life. Using metal-oxide semiconductors are very common because of many applications of them. Metal-oxide semiconductors such as SnO_2 [1,2], ZnO [3], In_2O_3 [4], Fe_2O_3 [5] and TiO_2 [6] are widely used for detecting small amount of target gas in air with which electrical resistance changes[7,8].Titanium Dioxide is one of the most popular oxide materials due to their superiorcharacteristics in various applications including photoelectrochemistry[9]. Band gap of TNPs is about 3.2 eV. Particularly, nanostructured TiO_2 have recently been of great interest because nanostructures often improve photocatalytic performance and /or exhibit properties different from bulk counterparts[9] .Titanium Dioxide is extensively used because of its some important properties like high refractive index , non-toxicity and chemical inertness in the presence of acid and basic environment due to these properties it has many potential applications in photocatalysis, polymer industry, white pigment [10] and gas sensor and corrosion protection coating[11]. Titanium Dioxide nanoparticles are prepared with different methods like electrical arc discharge [6], micro emulsion, chemical bath, sol-gel and etc. TiO_2 exists in three phases: rutile, anatase and brookite. Both rutile and anatase have tetragonal crystal structure and brookite has orthorhombic structure. Anatase is a useful catalyst in photochemistry because of its high photoactivity and rutile are common white pigment being employed for its superior optical hiding power, [12]. Both crystalline TiO_2 phases can be obtained by claiming the amorphous phase at different temperatures, [12]. In this study we synthesis TiO_2 nanoparticles by sol-gel method because of its simple set up, inexpensive and quick process. For anatase phase, we calcined powder at 450°C. One of TNPs applications is as gas sensing [13].Porous silicon (Ps) has recently been discussed as a novel material for chemical sensors and biosensors applications on account of its large specific area and its high reactivity [14]. Many parameters of Ps are reported to vary as a function of a change in the gas environment for example the intensity of Photo Luminescence (PL), the dielectric constant of the porous layer the conductance and the resonance frequency of a Fabry-Perot resonator made up of Ps. The pore size in the electrochemically synthesized Ps can be easily adjusted between few nanometres to several micrometers by choosing appropriate etching conditions [15].

We used porous poly silicon for gas sensor device. We used Poly silicon because of its important role in electrical industry [15]. One method of introducing pores in silicon is through the use of an anodization cell. Possible anodization cell employs Platinum cathode and Silicon wafer anode immersed in Hydrogen Fluoride (HF) electrolyte. Corrosion of the anode is produced by running electrical current through the cell. In this study we could obtain homogeneous porousity by poly silicon in range of 24 nm to several micrometer. Nanoporous metal oxides offer the advantage of providing large sensing surface areas for detecting ppm or ppb range of gases like CO_2. The ratio of c/a in anatase phase is 4 times larger than rutile phase which shows that anatase lattice detect more gas in comparing with rutile lattice. The sandwich configuration was used as gas sensor. Gas sensors are operated by different mechanisms which can be divided into two main categories based on chemical and physical behaviours of the sensing materials.

In this report, DC and AC electrical properties of AL/Si /Ps/TNPs/AL (sandwich device) were obtained in presence of CO_2 gas and effect of TiO_2 nanoparticles on sensitivity of gas sensing in presence of CO_2 gas. To sense the existence of gases [16]. The advantage of PS gas sensors over metal oxides is that PS gas sensors work at room temperature. A disadvantage of Ps gas sensors is that its ability for respond to just a few gases like organic vapours [17, 18, 19-21], humidity [19, 20, 22], NO and NO_2 [23–26], NH_3 and HCl [26]. In order to Ps to respond to

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other gases or to increase its sensitivity, one choice is to cover the surface of Ps by a thin layer of catalyst.

Experimental Details

$Ticl_4$ (Merck) and propanol (Merck) were used as precursor materials to synthesis of TiO_2 nanoparticles by sol-gel method. A solution of $TiCl_4$ and propanol in the proportion of 1:10 respectively, was stirred continuously in 500 rpm speed for 30 mins at room temperature. Then it was dried at 100 $^{\circ}$C in oven and anatase TiO_2 nanoparticles was produced by calcined at 450°C for 2 hours. Gas sensor device was made upon following instruction: The nanoparticles which in homogeneous and narrow distribution size were deposited on poly porous silicon plate substrate. Poly silicon was poroused by chemical electrolysation method with electrolyte solution that was included HF and C_2H_5OH in ratio of 1:6, respectively. Current of electrolysation was 7 mA for 20 mins. The anode was AL/Si and cathode was platinum. The average pores size was in range of 24 nm to 5 µm. Then TNPs was deposited on porous poly silicon plate by Electron Beam Gun in 10^{-5} pressure at room temperature. The thickness of layer has been deposited was 23 nm. This Device was made in sandwich form. The Device by two Aluminum electrodes were deposited under and top of device by Electron Beam Gun in same condition of TNPs deposition.

TNPs was characterized by X-ray diffraction with an Eqinox 3000 made by France, using CuK_{α} radiation, an accelerating voltage of 40 kV and emission current of 25 mA were employed. The surface morphology of TNPs was observed through Field Emission Scanning Electron Microscope (FESEM) with a Philips model XL30 instrument made in Holland. Light absorption spectroscopy analysis with Perkin-Elmer UV-vis Spectrometer was also performed. The surface morphology of porous poly silicon was observed through scanning electron microscope too.

Results and discussion

Surface morphology of TNPs were carried out by FE-SEM technique where is shown in fig.1.it shows that particles are homogeneous and spherical with narrow size distribution.

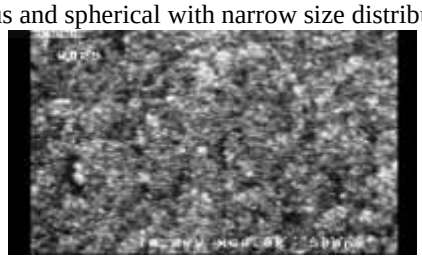

Fig.1. FESEM image of TiO_2 nanoparticles

X-ray diffraction from TNPs in fig.2 Shows that all of peaks confirm that sample is purity nanocrystalline anatase phase in comparing with standard TiO_2 anatase (card number 21-1272). Size of nanoparticles was calculated by using Scherrer's formula for the corresponding X-ray spectral peaks. The full width at half maximum (FWHM) of the sample peaks are extended by decreasing the size of particles [27].

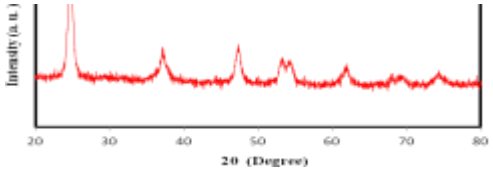

Fig.2. XRD pattern from TiO_2 nanoparticles

In fig.3 UV-vis spectroscopy analysis was also performed. The spectra shows that the absorbed wave length in about 293 Aº and band gap of TNPs was calculated about 3.26 eV. While band gap of bulk TiO_2 is 3.32 eV. The difference illustrated that effects of the quantum size on optical properties were greater than that of the coulomb band surface polarization [27].

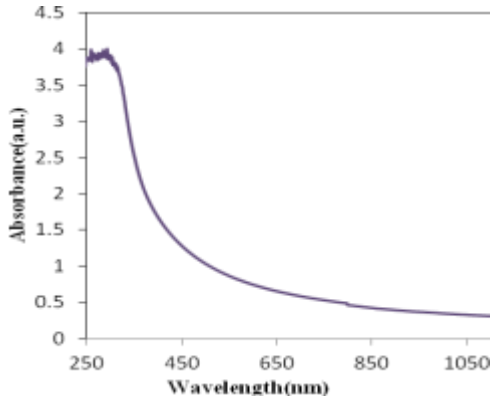

Fig.3.UV-vis spectroscopy

Fig.4. shows FESEM image of porous poly silicon. Porousity was performed by chemical electrolysation. Image confirmed that the pores are almost homogeneous with 5µm in pore size inspire hard homogeneous porousity for poly silicon.

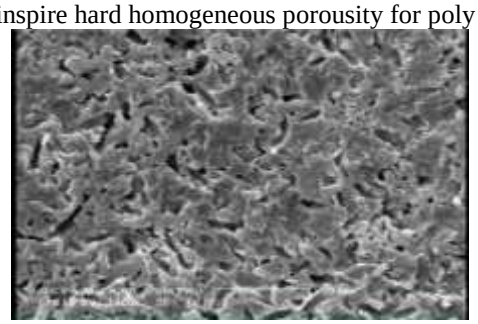

Fig.4.FESEM image from porous poly silicon

I-V curves in fig.5 show different positions of device in presence of CO_2 gas and without gas at room temperature. It shows that in presence of CO_2 gas, the devices with TNPs current (was measured by Keithley 61OC INSTRUMENTS) increased by increasing voltage. Due to small band gap of TNPs, by acting voltage, enough energy was made to excite the electrons from valence band to conducting band and left holes in valence band where cause to increase in current,[28]. In other hand, because of shotky junction between TNPs and porous poly silicon by increasing in voltage, the resistance of junction was decreased, thus the current was increased.

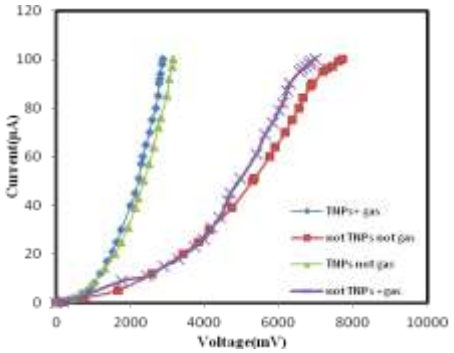

Fig.5. I-V curves in different conditions for device.

C-f plot was drawn in fig.6 at room temperature that device by TNPs, in presence of CO_2 gas by increasing frequency, capacity (was measured by MT 4080LCR Meter) decreased.

Semi-intrinsic conductivity inside of nanocrystallin paths in low frequencies, the space-charge limited conduction (SCLC) controlled by DC bias and hopping transferring on irregular porousity structure in high frequencies, are the factors that effect on conductivity,[29].

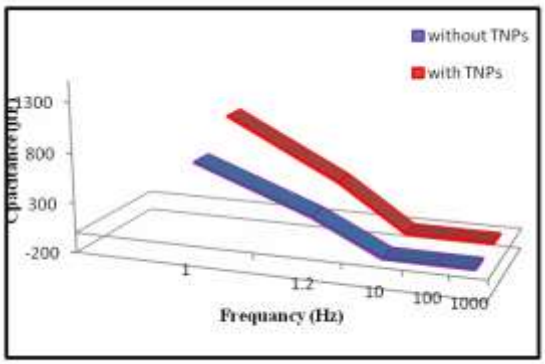

Fig.6.C-f plot for different conditions at room temperature

I-t plot was shown in fig.7 that shows sensitivity of sensor. The optimum temperature for device working was calculated at 380 K. At this temperature in presence of CO_2 gas, current increased by passing time, when air is reintroduced, previous sensor current value is recovered. Slow desorption of adsorbed CO_2 molecules cause to slow recovery time. It can be find that AL/Si/Ps/TNPs/AL is sensitive and reversible device to sensing CO_2 gas at 380 K temperature.

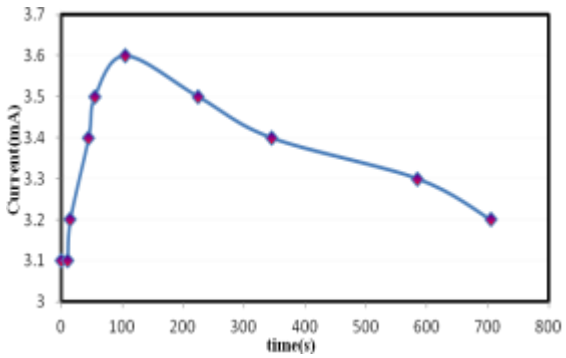

Fig.7. I-t plot for sensor

Conclusion

In this study, TNPs was prepared by sol-gel method and was deposited on porous poly silicon by chemical electrolysation and AL/Si/PS/TNPs/AL sandwich device was made by Electron Beam Gun deposition with two AL electrodes. Investigating electrical properties sensitivity of CO_2 gas at room temperature, confirmed that TNPs increase gas sensitivity and current at room temperature and capacity but by in presence of gas, capacity decreased. AL/Si/PS/TNPs/AL device is a sensitive CO_2 gas sensor at room temperature and reversible sensor at optimum temperature that hasn't reported yet.

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