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RESEARCH ARTICLE

Hydrothermally Synthesized NanoTiO_2 Thick Films for Gas Sensing Application

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Abstract: TiO_2 nanoparticals were prepared by hydrothermal synthesis technique. The thick films of TiO_2 were prepared by screen printing technique; gas sensing performance of this film was tested for various gases. The film showed highest response and selectivity to H_2S gas. The gas response selectivity of film were measured and presented. The films were characterized by x-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Selected Area diffraction and optical absorption spectroscopy technique. The quick response and fast recovery are the main features of these films. The effect of temperature on the optical, structural, morphological and gas sensing properties of the films were studied and discussed.

Keywords: TiO_2, Hydrothermal synthesis, Thick films, Gas sensor, Screen-printing technique

Introduction

Accompanying the acceleration of urbanization and industrialization, air pollution has become one of the most serious environmental problems on earth. It affects not only human health but also the health of ecological system. The atmosphere protects life on earth by absorbing ultraviolet solar radiation, warming the surface through heat retention, and reducing temperature extremes between day and night. However, severe loss of stratospheric ozone has been detected in the high latitudes of the Northern Hemisphere as well as over the Antarctic. At the same time, intensification of ultraviolet radiation has been observed. Ultraviolet radiation is known to a danger to human beings as well as having an effect on agricultural, forests and water ecosystems.

Global air pollution studies have been an important topic. The observation and collection of reliable data on regional and global air quality has a rather brief history. Routine atmospheric measurements of gas and particle concentrations have been conducted at sites with ground based instruments.

Other amenities such as home appliances and security systems in combination with advanced electronics also utilize sensors to give outstanding performance. Similarly, sensors have been extensively used in the medical field for diagnostic and therapeutic purposes and also for environmental monitoring of pollution hazards. With the growing awareness of the harmful effects of industrial wastes, emissions from vehicles exhausts, *etc*., various types of sensors are necessary as pre-requisites to detect these toxic pollutants before converting them into harmless products.

In the recent research sensors have attracted a great deal of attention from scientists and engineers. Even in the near future, it is expected to gain important in view of the construction of more or less intelligent ensembles, which integrate actuating, sensing and computing subsystems. Detection of various gases using solid state chemistry has generated a great deal of interest, both in academia and in industry.

The catalytic, electronic and optical properties of TiO_2 made it an important material for application such as dye sensitized solar cell[1,2], sensor[3], photocatalysis[4,5] and photo splitting of water[6]. The electronic properties depend on their atomic structure and shape of TiO_2.

Experimental

The TiO_2nanoparticles were synthesized by a hydrothermal process and using commercial Ti(IV) isopropoxide powder (98% fromAcros Organics) as source material. In detail, 3.6 g of Ti isopropoxide powder was mixed with 100 mL of water and stirred at room temperature. Isopropoxide immediately hydrolyzed, forming an amorphous precipitate. The suspension was repeatedly centrifuged, filtered and washed with distilled water. Finally, after last filtration, 160 mL of distilled water was added for hydrothermal experiments. The mixture was put into a Teflon-lined stainless autoclave which was heated at 180 ^oC for 12 h, after that it was naturally cooled down to room temperature. The obtained precipitation was filtered and washed in deionized water.

The thixotropic paste[7-10] was formulated by mixing the fine synthesized power of TiO_2 with solution of ethyl cellulose (as temporary binder) and organic solvents. The paste was screen printed on glass substrate in desired patterns; the prepared films were fired at 550 ^oC for 30 min.

The sensing performance of the thick films was examined by using a static gas sensing system[11,12]. To heat the sample up to required operating temperatures, the heater was fixed on the base plate. A thermocouple is connected to a digital temperature indicator for temperature measurement. The required gas concentration inside the static system was achieved by injecting a known volume of test gas using a gas-injecting syringe.

Results and Discussion

Microstructural analysis by using SEM

The micro structural and chemical compositions of the films were analyzed using a scanning electron microscope (SEM, JEOL JED 6300) coupled with an energy dispersive spectrometer (EDS, JEOL JED 2300LA).

Figure 1 depicts a SEM image of TiO_2 thick film fired at 550 ^oC. The film consists of voids and a wide range of particles distributed uniformly.

UV-Visible spectroscopy analysis

Figure 2 shows the UV-visible spectra of hydrothermaly synthesized TiO_2 powder.This spectra of TiO_2 is the wavelength range of 150-800AU. The maximum absorbance is 0.8 for

wavelength 328AU and band gap is 3.74eV. The TiO_2 exists in three different crystals modifications, that is as anatase (tetragonal crystal structure with 3.2eV energy gap[13]), rutile (tetragonal crystal structure with 3.2eV energy gap), and brookite (orthorhombic with 2.96eV energy gap). Among the three phases rutile is most stable phase, which can be hydrothermally prepared.

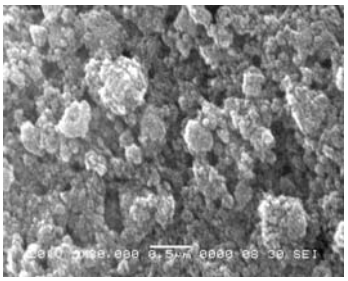


Figure 1. SEM image of thick film

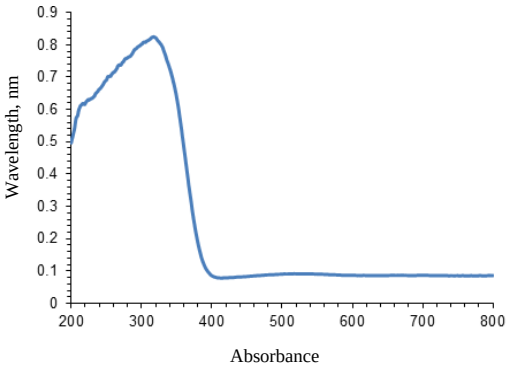
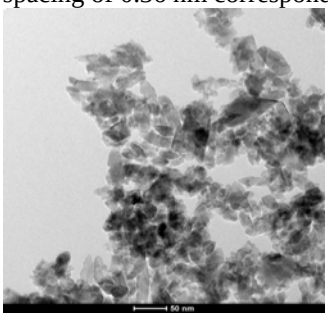


Figure 2. UV-visible spectra of synthesized TiO_2 powder

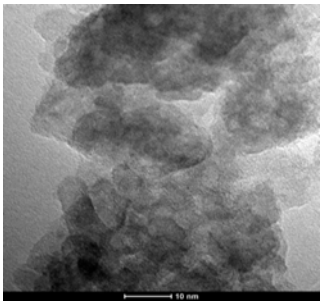
TEM and SEAD analysis

Figure 3(a) and (b) shows TEM images of hydrothermaly synthesized TiO_2. It has been observed that the rice grain shape nanocrystallite TiO_2 showed an agglomerated status, where magnified image. Figure 3(b) shows atoms are arranged in definite manner and d spacing is 0.36 nm.

Figure 4 shows selected area diffraction pattern, reveals that TiO_2 is predominantly single crystalline anatase[14]. The lattice-resolved image shown in Figure 4 with lattice spacing of 0.36 nm corresponding to the prominent (101) plane.



(a)



(b)

Figure 3. TEM imagesof synthesized TiO_2 powder

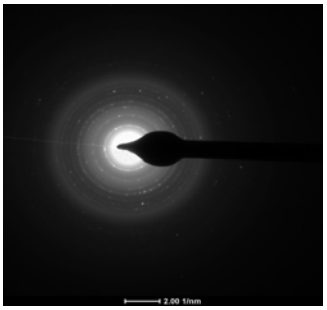


Figure 4. SEAD of synthesized TiO_2 powder

X-Ray diffraction analysis

Figure 5 shows the x-ray diffraction pattern of hydrothermally synthesized TiO_2.The pattern is well matches with PDF 01-070-2556 data[15]. The sharp pecks indicate that TiO_2 is well crystalline; the % crystallinity is 93.3%. The average grain size was determined by using Scherer formula and was estimated to be 262 nm.

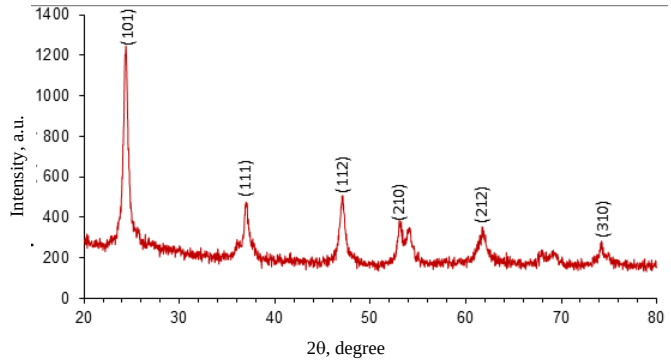


Figure 5. X-Ray diffraction pattern of TiO_2

I-V characteristics of TiO_2 thick films

Figure 6 Shows the I-V characteristics which represent variation of electric current (pA) *versus* change in voltage (volt) across the thick film of the TiO_2 thick film at room temperature. It has been noted from the graph that the contacts fabricated on the film were ohmic in nature.

Electrical conductivity

Figure 7 represents the variation of conductivity with temperature for pure films. It is clear from the graphs that the conductivity is varying approximately linearly with temperature. Conductivity of the films goes on increasing with an increase in temperature. Hence resistivity goes on decreasing with increase of temperature. Therefore, material exhibit negative temperature coefficient of resistance (NTC).

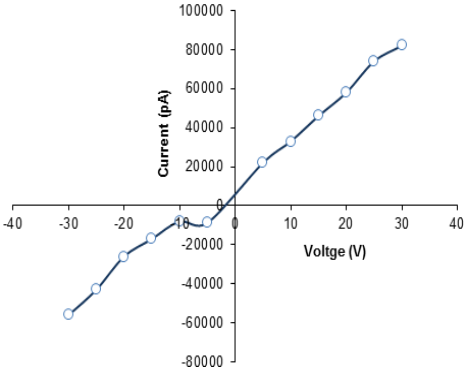


Figure 6. Variation of electric current *versus* applied voltage graph of TiO_2 thick film

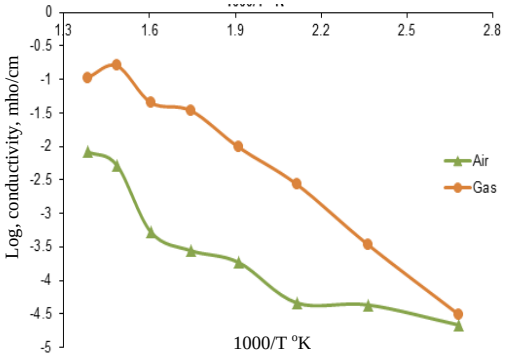


Figure 7. Variation of electrical conductivity with temprature

Sensitivity of TiO_2 films

The gas sensing performance of TiO_2 thick films were studied by using static measurement system. The conductance of TiO_2thick film resistors were measured by means of conventional circuitry by applying constant voltage and measuring the current by Pico ammeter as a function of temperature in air as well as in CO, CO_2,H_2,NH_3,Cl_2,H_2S, LPG, gas atmosphere (800 ppm concentration). The operating temperature was varied at the interval of 100 ^oC up to 450 ^oC. From the measured conductance in air as well as in gas atmosphere, the gas response was determined at particular operating temperature using the equation 1.

$$S = \frac{(G_{gas} - G_{air})}{G_{air}} \quad (1)$$

Where G_{air}= Conductance of sensor in air medium.
G_{gas}= Conductance of sensor in gas medium

Figure 8 shows the variation of sensitivity of TiO_2 films to H_2S gas(1000 ppm) with operating temperature ranging from 100 to 450 ^oC. The response goes on increasing with operating temperature, attains its maximum (122) at 300 ^oC and then decreases with a further increase in operating temperature.

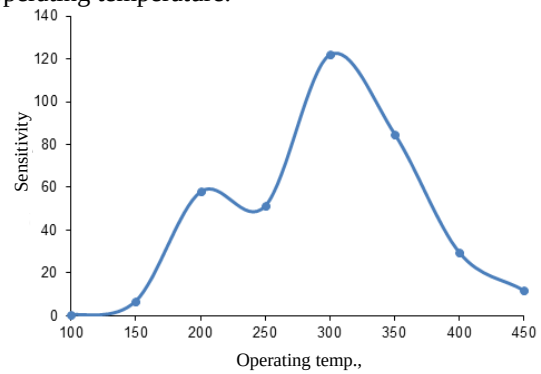


Figure 8. Variation of sensitivityof TiO_2 films to H_2S gas

Selectivity of TiO_2 thick films for various gases

Figure 9 shows the histogram of the selectivity of TiO_2 thick film for various gases. The TiO_2 thick films were selective to H_2S gas against the other tested gases at 300^oC.The sensitivity of thick films were 122 for H_2S gas.

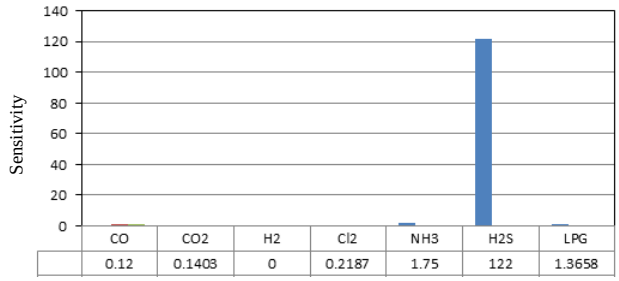


Figure 9. Selectivity of TiO_2thick film

Sensitivity of thick film by varying H_2S gas concentration

Figure 10 shows the sensitivity of TiO_2 thick film by varying H_2S gas concentration (ppm).The film shows maximum sensitivity for 1000 ppm to H_2S gas. The sensitivity increases with gas concentration but decreases feature due to saturation.

Gas sensing mechanism

The gas sensing mechanism belongs to the surface controlled type which is based on the change of the electrical conductance of the semiconducting material upon exposure to H_2S gas. The gas sensitivity is a function of grain size, surface state and oxygen adsorption.

The surface area generally provides more adsorption-desorption sites and thus the higher sensitivity. The H_2S sensing mechanism is based on the change in conductance of TiO_2 thin film, which is controlled by H_2S species and the amount of chemisorbed oxygen on the surface. It is known that atmospheric oxygen molecules are adsorbed on the surface of semiconductor oxides in the form of O^{2-}, O^- or O^{--}.

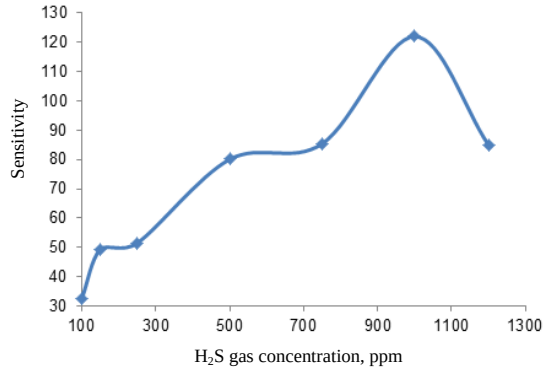


Figure 10. Sensitivity of thick films by varying H_2S gas concentration

The reaction kinematics may be explained by the following reactions:

$$O_2(RT) \rightarrow O_{2^-} \text{ (up to } 200^oC) \rightarrow 2O^- \text{ (up to } 400^oC) \rightarrow 2O^{2-} \text{ (above } 400^oC) \quad (2)$$

$$O_2 + 2e^- \rightarrow 2O^-ads \quad (3)$$

On contact with the gas being sensed.

$$G + O^-ads \rightarrow GO_{des} + e^- \text{ (desorbed)} \quad (4)$$

The presence of chemical adsorbed oxygen could cause electron depletion in the thin film surface and building up of Schottky surface barrier; consequently, the electrical conductance of the thin film decreased to a minimum. The TiO_2 thin film interacts with oxygen by transferring the electron from the conduction band to adsorbed oxygen atoms. The response to H_2S can be explained as a reaction of gas with the O_2 (ads)–.

$$H_2S + 3O \text{ (ads)} – H_2O \text{ (g)} + SO_2 \text{ (g)} + 3e– \quad (5)$$

With this reaction, many electrons could release to thick film surface. This could make the Schottky surface barrier decrease; with the depletion layer thinner; consequently, the electrical conductance of the thick film increases as shown in Figure 11.

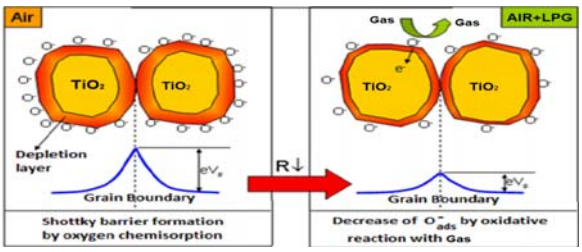


Figure 11. Gas sensing mechanism

More gas would be absorbed by the thick film surface; consequently, the gas sensitivity was enhanced. Increase in operating temperature causes oxidation of large number of H_2S molecules, thus producing very large number of electrons. Therefore, conductivity increases to a large extent.

This is the reason why the gas sensitivity increases with operating temperature. However, the sensitivity decreases at higher operating temperature, as the oxygen adsorbents are desorbed from the surface of the sensor[16]. Also, at higher temperature, the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for decreased gas sensitivity at higher temperature[17].

Conclusion

The rice grains-shaped TiO_2nanostructucturs were synthesized by using hydrothermal method. Anatuse is found to be a predominant phase. Powder XRD shows grain size 174.6 nm and % crystanillity is 93.3%.Increse in band gap represent formation of nanostructure. The thick films are prepared by using screen printing techniques. The thick films are sensitive to H_2S gas against all other tested gases.

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