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ARTICLE

Exclusive H₂S Detection with Greater Response Using Thermally Evaporated Titanium Oxide Film

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A B S T R A C T

The preparation of titanium oxide films using economically viable and mass scalable thermal evaporation technique is proposed with greater selectivity and response to toxic H_2S gas sensing. Crystalline phase and surface chemistry of the film was revealed using X-ray diffraction and X-ray photoelectron spectroscopy. Film samples with different thicknesses were prepared ranging from 50 to 300 nm for sensing measurements. Amongst these, film with 200 nm thickness was found highly sensitive to H_2S at 100 °C sensor operating temperature, whereas insensitive to other test gases under study. In addition, these films detect H_2S concentration of as low as 1 ppm.

I N T R O D U C T I O N

In recent years, economically viable toxic gas sensors are in great demand in many industries and laboratories. Hydrogen sulfide (H_2S) is one of the dangerous and life fatal gases as its leakage poses potential danger to the mammalian kingdom [1]. Semi-conductor oxides such as TiO_2 [2], ZnO [3], SnO_2 [4] and NiO [5] have showed potential as sensing materials for a wide spectrum of gases due their fascinating properties and stability. Nevertheless few of them are appropriate for realization of sensor technology unless modified or doped by another materials. Doping and modifications have its own technical issues. Thus, investigating new ways to develop undoped or unmodified materials is an extremely important to comprehend a robust and low-cost sensor technology.

Beldikyan *et al.* [6] investigated optical properties of TiO_2 thin films fabricated by thermal evaporation on glass, quartz and silicon. Gridzicki *et al.* [7] prepared high quality TiO_2 nanocrystalline films by reactive evaporation on Si substrate which exhibited hydrophobic behaviour. Au-TiO_2-NiO composite films for H_2S sensing were reported by Gaspera *et al.* [8] but showed low sensitivity. Pt-TiO_2 nanocrystals showed the response of ~70 towards 250 ppm H_2S/air at 500 °C [9]. Chaudhari *et al.* [10] reported TiO_2/Al_2O_3/Pd composite electrodes for H_2S sensing with poor sensing performance towards 200-1000 ppm at 225 °C. Mogal *et al.* [11] detected H_2S by thicker films with a sensor response (SR, %) ~ 100. Another

TiO$_2$ based H$_2$S sensing was reported by Topalian *et al.* [12] who detected low concentrations of H$_2$S by noise spectroscopy under UV light. Upon critical review of the literature in the field of TiO$_2$ films based H$_2$S sensors [13], none of the above reports were observed exclusively on undoped TiO$_2$ that explore the possibility of commercializing low-cost H$_2$S sensor technology. The present work deals with the fabrication of undoped TiO$_2$ films of different thicknesses by cost-effective thermal evaporation method for the gas sensing application.

E X P E R I M E N T A L

Fabrication of sensors: TiO$_2$ thin films of various thicknesses ranging from 50 to 300 nm were deposited on to the glass substrates using thermal evaporation technique (Hind Hivac, 12A-4H). Prior to this, glass substrates were cleaned by ultrasonicating in organic solvents such as trichloroethylene, acetone and methanol. Thermal evaporation of pure Ti wire at air base pressure of 2×10^{-5} mbar was performed. Further, samples were oxidized at 500 °C for 6 h under O$_2$ atmosphere to obtain TiO$_2$ thin films.

Sensor characterization: X-ray diffraction measurements were carried out by powder diffractometer (Proto manufacturing) to reveal the nature of crystalline phase of the films. X-ray photoelectron spectroscopy (XPS) measurements were performed using MgK$_\alpha$ source (RIBER, 133.137 Boulevard National 92503 system) at room temperature to investigate the surface electronic structures. All raw binding energies were corrected with C1s value, 285 eV. The spectra were fitted using a Shirley type background function using software XPSPEAK 4.1.

Gas sensing measurements: The gas sensing measurements were performed in a home-made static gas sensing set up. The sensor operating temperature was monitored and controlled by temperature controller circuit with Pt-50 attached at the backside of the film for heater and Pt-100 temperature reader. The electrical contacts were made by connecting silver wire using silver paint for charge transport. Then sensor was mounted in the 250 mL capacity stainless steel chamber. To calculate the response kinetics of the film, the known concentration of particular gases to be detected were injected inside the chamber using micro syringe. Keithley made 6487 picoammeter/voltage source and personal computer with Labview software were used to measure and record the response when the films were exposed to the gas. Sensor response (SR %) was calculated from the response curves using the formula:

$$SR\ (\%) = (I_g - I_a)/I_a \times 100 \qquad (1)$$

where, I$_a$ is the initial value of current when sensor in air and I$_g$ is the final value of current reaches saturation on exposure of gas. The response and recovery times of films were calculated from recorded sensing data. Response time was the time needed to reach 90 % of total change in current upon exposure to test gas. Recovery time was the time required to return to 10 % of its original baseline signal upon removal of test gas.
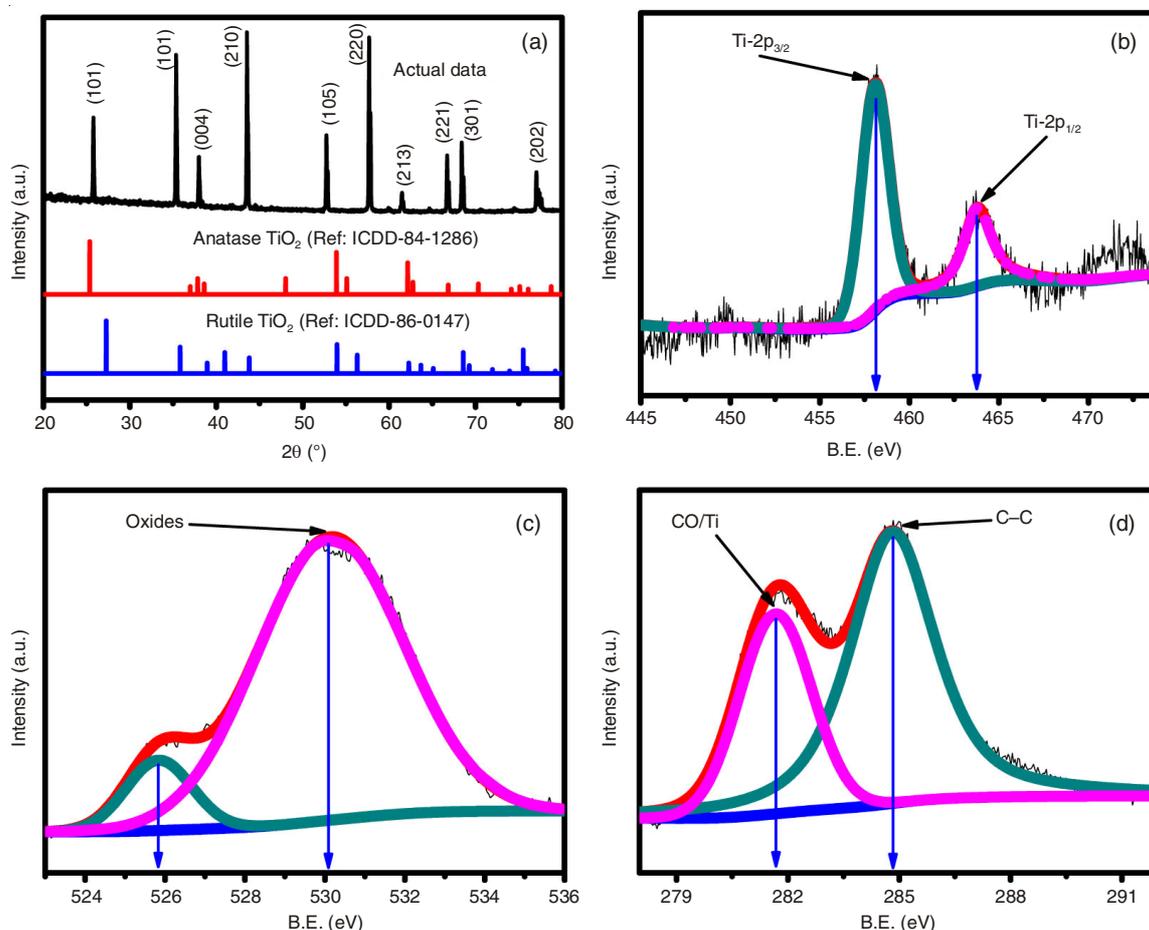
Fig. 1. (a) XRD pattern of titanium dioxide, (b) XPS spectra of Ti-2p, (c) O1s and (d) C1s of the film

R E S U L T S   A N D   D I S C U S S I O N

Sensor characterization: The XRD data of the films were taken for the range 20 to 80° as shown in Fig. 1(a). The obtained peaks belong to both the anatase (ICDD Card No.: 84-1286) and rutile phase (ICDD Card No.: 86-0147) which confirmed the formation of mixed phase. Fig. 1(b) summarizes the XPS results of the films prepared on glass substrates. The C1s peak at 281.8 eV corresponds to carbon atoms in carbidic states and other peak at about 285 eV is used as reference [14]. The Ti $2p_{3/2}$ & $2p_{1/2}$ core levels for titanium dioxide were seen to appear at 458 and 463.7 eV, respectively with the peak separation of 5.7 eV revealing Ti in +4 state. Also, both Ti core-levels are symmetric in nature ruling out the possibility of reduced species like Ti^{2+} or Ti^{3+}. The O1s core-level was deconvoluted using two Gaussian curves. The first is positioned at 526 eV with small contribution and other with significant contribution at ~530 eV as shown in Fig. 1(c). In general the relative order of O1s binding energy from 526 to 532 eV in a series of the same type of compounds is $O^{\delta-} <$ M-O < M-OH. From this fact the peak positioned at higher binding energy is attributed to M-O and another on lower binding energy is due to adsorption of partially charged oxygen species ($O^{\delta-}$) [15]. It is well-known that reactivity and surface electronic structure of the film is affected by the coordination of surface atoms with adsorbents.

Sensing properties of undoped TiO₂ films: TiO₂ films of thickness 200 nm were tested for different oxidizing and reducing gases such as H_2S, CO, NH_3, NO, C_4H_{10} and a change in current of the film as a function of time was recorded at different temperatures. It exhibits high selectivity towards H_2S gas and gave sensor response (SR %) equal to 30000 towards 50 ppm of H_2S concentration at sensor operating temperature of 100 °C and applied voltage of 0.1 V as shown in Fig. 2. A prominent feature of the TiO₂ film was its very fast response rate about a min on turning on the H_2S, showing switching
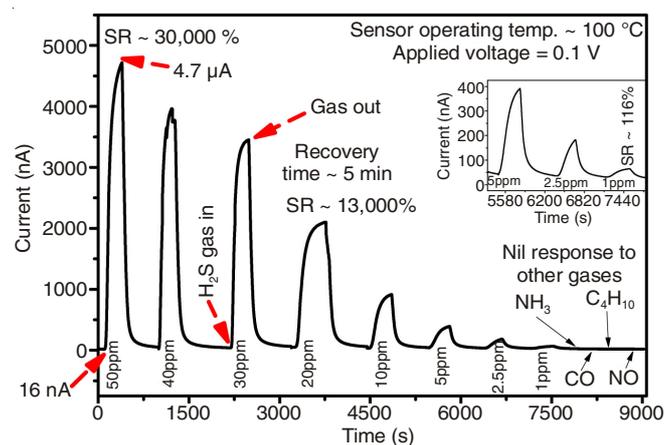
Fig. 2. Sensor response of undoped TiO₂ film with selectivity curve
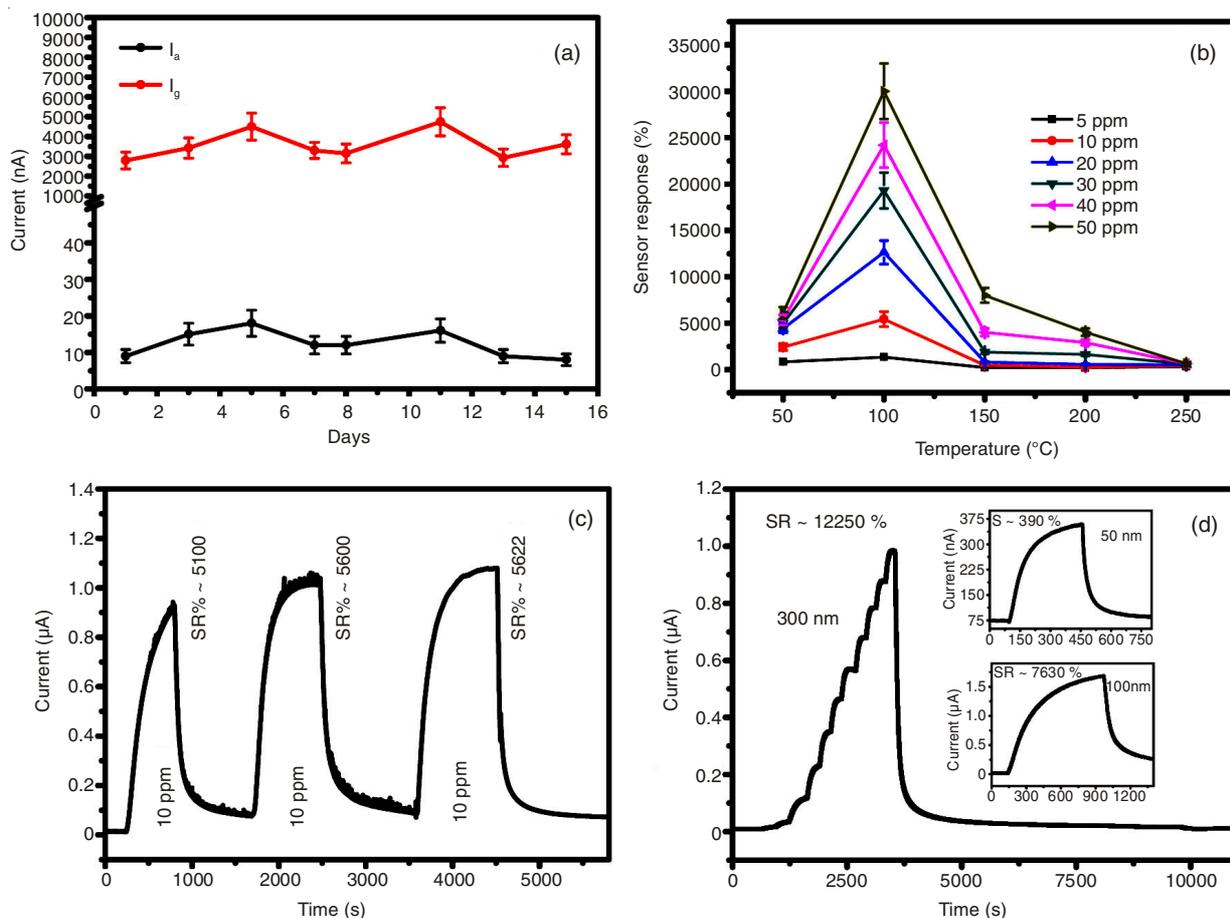
Fig. 3. (a) Stability data over a period of 2 weeks upon repetitive exposure towards 50 ppm of H₂S, (b) Sensor response at different temperatures with varying gas concentrations, (c) Sensor response curves recorded upon repetitive exposure of 10 ppm of H₂S and (d) real-time sensor response at different thicknesses of film

like response and recovery in about 5 min. This film was also sensitive at lower concentration and showed sensor response equal to 116 % at 1 ppm of H_2S concentration.

The long term stability measurement as shown in Fig. 3(a) indicated that value of current is almost stable over the measurement period of 2 weeks. No significant variations in the response values were observed indicating stable behaviour of the sensor. Fig. 3(b) shows sensor response of TiO_2 thin film at different temperatures with various gas concentrations informing optimized sensor operating temperature is 100 °C.

Fig. 3(c) shows the response curves recorded upon repetitive exposure to 10 ppm H_2S. The sensor exhibited nearly similar response values with almost identical response kinetics supporting its repeatability character. Fig. 3(d) shows variation of sensor response with different thicknesses of the film which revealed that the film of 200 nm thickness have showed much better response. The film of thicknesses 50, 100 and 300 nm showed responses of 390, 7630 and 12250 %, respectively.

Sensing mechanism: XPS studies showed existence of the partially charged "$O^{\delta-}$" oxygen species on film surface that play a major role in good H_2S gas sensitivity. As the oxidation potential of chemically adsorbed "$O^{\delta-}$" oxygen species are higher, allowed to accept electrons from oxide surface thereby creating electron-deficient layers. During sensing phenomena, when the H_2S reacts with these oxygen species, releases electrons thereby reduces thickness of depletion layer that facilitates charge transport in film which was evident on sharp decrease in the resistivity of the film, *via* following hypothesized reaction:

$$2H_2S_{(g)} + 2^\bullet O_2^{\delta-}{}_{(ads)} \longrightarrow 2H_{2(g)} + 2SO_{2(g)} + 3e^- \qquad (2)$$

So, the interaction with the H_2S is basically dominated by the nature of adsorbed oxygen species "$O^{\delta-}$" which is the unique strength of titanium dioxide films under investigation. The following schematic supports the H_2S sensing mechanism of thin films (Fig. 4).
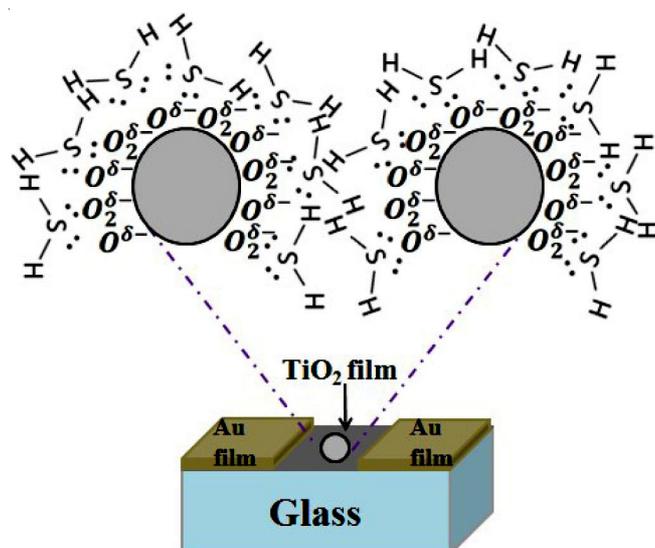
Fig. 4. H_2S gas sensing mechanism by titanium dioxide film made on glass substrate

Conclusion

Cost-effective titanium dioxide film sensors were successfully fabricated by thermal evaporation method. The XRD measurements revealed the formation of mixed (anatase + rutile) phase TiO_2 whereas XPS confirms the existence of chemisorbed partially charged oxygen species "$O^{\delta-}$" on film surface. The sensing measurement data demonstrated a high H_2S response (SR % ~ 30000) for 200 nm films at 100 °C sensor operating temperature with quicker response and recovery with better stability supporting its suitability for realization of H_2S sensor technology.

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