Hexamethylenetetramine-mediated TiO₂ films: Facile chemical synthesis strategy and their use in nitrogen dioxide detection

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Abstract

Hexamethylenetetramine (HMT)-mediated rutile and polycrystalline TiO₂ films are directly grown on a glass substrate by a simple chemical wet deposition method at ambient temperature. After confirming the crystallinity, phase-purity and surface morphology, as-grown TiO₂ films were explored for a variety of target gases including nitrogen dioxide, methanol, ethanol and ammonia at different temperatures for confirming the sensor application potential. The TiO₂ film shows a maximum response of 43% to 100 ppm NO₂ @ 180°C with fast response time of 16 s. In addition, the TiO₂ sensor film has potential to detect concentration of NO₂ as low as 10 ppm.

Keywords: Titanium dioxide; Nanoparticles; Microstructure; Gas sensor

1. Introduction

Recently, semiconducting metal oxides have attracted considerable attention in the gas sensing field owing to their low-cost, flexibility in production, availability of easy synthesis methods, high sensitivity, higher temperature stability, etc. [1-10]. Comprehensive introductory and technological efforts have been committed to fabricate perfect gas sensors based on different semiconducting metal oxides such as ZnO [5], TiO₂ [6], NiO [7], In₂O₃ [8], WO₃ [9], and Fe₂O₃ [10]. Amongst different metal oxides, *n*-type semiconducting TiO₂ is being considered as one of the most promising materials in gas sensing application due to its selectivity to target gases, mechanical robustness, and chemical stability at high temperatures [1-3, 6]. Hazardous nitrogen dioxide (NO₂) is basically an oxidizing gas, capable of damaging cells in the respiratory track and is also responsible for ground-level ozone layer. Home

heaters, gas stoves, and high-temperature combustion processes (trucks, cars and power plants) release substantial amounts of gaseous NO₂ every day [4, 9]. Therefore, in order to design gas sensing systems, the development of sensing materials, which detect hazardous NO₂ at low concentration, is essential. It was reported that, most of TiO₂ film-based NO₂ gas sensors need higher operating temperatures (T>250°C) [11-13] and, moreover, in about 90% of the cases, synthesis of TiO₂ films was done in powder form and not via a direct approach. Till date there is no report, where the development of hexamethylenetetramine (HMT)-mediated chemical synthesis of direct rutile and polycrystalline TiO₂ films is achieved and used for the detection of NO₂ or other target gases. Thus, in present work, we made an attempt to prepare TiO₂ films directly onto glass substrate using a wet chemical method and used it for detecting NO₂ concentration with fast response time. The results obtained in this work found novelty in; synthesis, lower NO₂ detection, and low operating temperature than that of reported study on TiO₂ films [11-13].

2. Experimental

In typical experiment, 2.5 ml of TiCl₄ and 0.03 g of HMT were mixed in a 100 ml beaker, containing 47.5 ml of deionized water. The resulting mixture was stirred for 10-15 min at room temperature until the solution became transparent. Ultrasonically cleaned glass substrates were immersed vertically in the desired mixture and the reaction was allowed to proceed for 3 h at 338 K in a digitally controlled water bath. After the reaction, whitish colored films were observed, which were removed and washed with distilled water in order to avoid loose particles and annealed at 573 K for 3 h before being used for the gas sensing study. We have repeated the experiments two times for checking the accuracy and reproducibility. Gas sensing measurements on TiO₂ films were performed by using an airtight glass chamber having volume of 250 cm³ with the sensor coupled with a Keithley 6514 system electrometer [10]. The response (%) was calculated by using the following relation,

$$\text{Response (\%)} = [(R_g - R_a)/R_a] \times 100 \quad (1)$$

where, R_g and R_a are the resistance of the sensor film in presence of the test gas and air, respectively.

3. Results and discussion

Fig.1 (a) illustrates the X-ray diffraction pattern of TiO₂ film obtained from wet chemical method. The XRD pattern was found to be polycrystalline with a negligible amorphous fraction, as can be seen from high intensity, sharp peaks, of course belonging to the product itself. All observed diffraction peaks and corresponding planes are consistent with the rutile phase of TiO₂ (JCPDS data file No. 21-1276). The average crystallite size was calculated along the highly preferred (110) plane, using the Scherrer relation, was found to be ≈ 28 nm. The Raman

spectra of TiO₂ (Fig.1 (b)) showed four active modes at 142 cm⁻¹ (B_{1g}), 232 cm⁻¹ (E_g), 447 cm⁻¹ (E_g), and 610 cm⁻¹ (A_{1g}), respectively. The observed Raman active modes were of rutile TiO₂, containing both stretching and bending vibrations [14]. The Raman results signify that the TiO₂ phase mainly crystallizes in the rutile structure with Raman active modes of multi-phonon process [14, 15].

Fig.2 presents surface appearance of as-deposited TiO₂ films by various means. FESEM image (Fig.2 (a)) shows that the fused lumps of TiO₂ nanoparticles are randomly distributed on the substrate surface. Such kind of morphology is preferred for gas sensing applications, as it provides a larger surface area and fast diffusion paths through air-voids and edge-gaps for the target gas to interact with the sensing material [2, 10]. Transmission electron microscopy (TEM) images (Fig.2 (b, c)) clearly highlight the aggregated state of TiO₂ nanoparticles with an average diameter of ≈35 nm. The TiO₂ nanoparticles with porous characteristics would efficiently facilitate the gas diffusion, which dominate its sensing characteristics [2, 10]. Ordered lattice fringes were seen from the high-resolution TEM (HRTEM) image (Fig. 2 (d)), supporting the polycrystalline nature of as-synthesized TiO₂. The calculated lattice spacing along (101) plane was found to be 0.33 nm. From selected area electron diffraction (SAED) pattern (Fig. 2(e)), presence of several diffraction rings with dotted arrays was clearly seen; indicating a polycrystalline nature of synthesized TiO₂, again, supporting the XRD results.

Gas sensing performance of TiO₂ films in terms of change in resistance was carried out for different temperatures and gases (such as NO₂, ammonia, ethanol, and methanol). The selectivity study, shown in Fig.3 (a), revealed that the TiO₂ films were very sensitive towards NO₂ gas while the response to other test gases is quite limited. TiO₂ film exhibited the highest response of 43% to 100 ppm NO₂ @180°C and which is a ≈13 times greater than that of NH₃-the second ranking gas. For the optimization of working temperature of TiO₂ film, 100 ppm NO₂ was exposed to different temperatures and the subsequent results are displayed in Fig.3 (b), which proves that the TiO₂ film shows a maximum response to NO₂ @180°C. At lower and higher temperature, the response of sensor is limited due to the speed of chemical reaction and speed of diffusion of gas molecules, respectively. With increasing temperature, the response of the sensor decreases due to excess of temperature that shrinkage the gas diffusion close to the sensor film. But at intermediary temperature (herein 180°C) speeds of these two processes become equal and sensor exhibits its maximum response value [9, 10]. Fig. 3 (c) shows the variation of TiO₂ response as a function of different NO₂ concentrations. The obtained response values for 10, 20, 40, 60, and 100 ppm of NO₂ were 6, 8, 12, 31, and 43 % @ 180°C, respectively. Of note, the TiO₂-based sensor film is capable to detect low 10 ppm

concentration of NO₂ with 55 s response time. The plot of resistance vs. time for the TiO₂ film to 100 ppm NO₂ gas @180°C is shown in Fig. 3 (d). The increase in resistance upon exposure to NO₂ features a short response time of 16 s and a recovery time of 140 s upon removal of NO₂ gas from exposure chamber [Fig. 3 (d)]. The increase of resistivity can be explained with the following corroborations: When the *n*-type TiO₂ film (electrons as majority carriers) is exposed to air, oxygen molecules from the air adsorb on the TiO₂ surface, form the adsorbed oxygen species such as O₂⁻, O⁻, and O²⁻. When the oxidizing NO₂ molecules interact with the TiO₂ surface, the adsorbed oxygen is removed. As a result due to the electron accepting nature of NO₂, TiO₂ film resistance increases with the decrease in carrier concentration [9, 10].

In summary, HMT-mediated TiO₂ films were successfully synthesized by an easy wet chemical deposition method and their gas sensing activity was studied towards various toxic gases like nitrogen dioxide, methanol, ethanol, and ammonia. Structural and phase analysis, using XRD and Raman spectra, supported well for the formation of polycrystalline rutile TiO₂ films onto the glass substrate. Aggregated TiO₂ nanoparticles of nano-rods type with considerable porosity were grouped together, as confirmed from SEM and TEM images. Gas sensing results showed that the TiO₂ films were quite selective to NO₂ @ 180°C with a rapid response time. Besides, the TiO₂ films have an ability to detect NO₂ as low as 10 ppm. The attractive features of HMT-mediated TiO₂ sensor film could be its lower operating temperature, fast response time, and lower detection limit, making it a suitable material for the detection of hazardous NO₂ at various fields.

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References

- [1] Buso D, Post M, Cantalini C, Mulvaney P, Martucci A. Adv Funct Mater 2008;18:3843–9.
- [2] Djaoued Y, Ozga K, Wojciechowski, Reshak AH, Robichaud J, Kityk IV. J Alloy Comp 2010; 508:599-605.
- [3] Perillo PM, Rodriguez DF. Sens Actu B 2012; 171:639–43.
- [4] Park S, An S, Mun Y, Lee C. ACS Appl Mater Inter 2013; 5:4285–92.

- [5] Fu Y, Nie Y, Zhao Y, Wang P, Xing L, Zhang Y, Xue X. ACS Appl Mater Inter 2015; 7:10482–90.
- [6] Nisar J, Topalian Z, Sarkar A, Osterlund L, Ahuja R. ACS Appl Mater Inter 2013;5:8516–22.
- [7] Lee CY, Chiang CM, Wang YH, Ma RH. Sens Actu B 2007; 122:503–10.
- [8] Vomiero A, Bianchi S, Comini E, Faglia G, Ferroni M, Sberveglieri G. Cryst Grow Des 2007;7:2500–04.
- [9] Mane AT, Kulkarni SB, Navale ST, Ghanwat AA, Shinde NM, Kim JunHo, Patil VB. Cera Inter 2014;40:16495–502.
- [10] Navale ST, Bandgar D K, Nalage SR, Khuspe GD, Chougule MA, Kolekar YD, Sen S, Patil VB. Cera Inter 2013;39:6453–60.
- [11] Saruhan B, Yücel A, Gonullu Y, Kelm K. Sens Actu B 2013;187:586–97.
- [12] Esmaeilzadeh J, Marzbanrad E, Zamani C, Raissi B. Sens Actu B 2012;161:401–5.
- [13] Lu HF, Li F, Liu G, Chen ZG, Wang DW, Fang HT, Lu GQ, Jiang ZH, Cheng HM. Nanotechnology 2008;19:405504-11.
- [14] Porto PS, Fleury PA, Damen TC. Phys Rev 1967;154:522–6.
- [15] Navas J, Coronill A, Aguilar T, Santos D, Hernandez N, Alcantar R, Lorenzo C, Callej J. Nanoscale 2014;6:12740-57.

Figure captions

Fig.1. (a) XRD and (b) Raman spectrums of rutile TiO₂ film product.

Fig.2. (a) FE-SEM, (b) TEM (20 nm resolution), (c) TEM (10 nm resolution), (d) HRTEM, and (e) SAED images of rutile TiO₂ films.

Fig.3. Plots of; (a) selectivity study of TiO₂ film to various gases, (b) temperature dependant response of TiO₂ film to 100 ppm NO₂, (c) response as a function of different NO₂ concentration, and (d) change in TiO₂ film resistance upon 100 ppm exposure of NO₂ gas @180°C.

Fig.1.

Fig.2.

Fig.3.