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Effect of pyrolytic temperature on the properties of TiO_2/ITO films for hydrogen sensing

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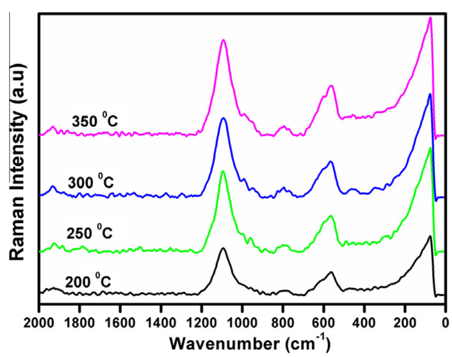
HIGHLIGHTS

- Promoting effect of ITO seeding layer resulted in *c*-axis oriented anatase TiO_2.
- Optical spectra revealed both direct and indirect transition.
- Hydrogen sensing response of the film increased with substrate temperature.
- Recovery is faster depending on crystallinity of the film.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium dioxide (TiO_2) thin films were prepared on ITO (222) coated glass substrates by spray pyrolysis technique. The influence of substrate temperature on the orientation, phase, vibrational bands and band gap energy of TiO_2 films were discussed. The X-ray diffraction patterns of the films revealed preferentially oriented (101) TiO_2 anatase phase at the substrate temperature of 300 °C and 350 °C. Fourier transform infrared spectra of the films showed the significant sharpening of absorption band at ~645 cm^{-1} with increase in substrate temperature, which clearly indicates the formation of anatase phase dependent on substrate temperature. Fourier Raman Spectra of the films showed the significant presence of long range order anatase TiO_2 phase. The optical measurements of the film prepared at different substrate temperatures revealed the direct band gap of 3.15–3.63 eV and indirect band gap of 3.48–3.73 eV, characteristic of TiO_2 anatase phase. To understand the enhancement of sensing performances of TiO_2 films with substrate temperature, the gas sensing mechanism of the films towards 400 sccm of hydrogen at room temperature was studied and discussed.

Introduction

Hydrogen is considered today to be an abundant material and a renewable energy source of the future because it provides zero hazardous emissions, renewable and easily available. Hydrogen fuel is used in large areas such as fuel cells in rocket propellants. In addition, chemical industries, food industry, and semiconductor industry use hydrogen as one of the processing components.

All these applications necessitate the development of hydrogen sensor devices which allow it to function safely. Since hydrogen is explosive above the lower explosion limit, special safety precautions are set, and devices which permit the detection of hydrogen presence become indispensable [1]. Titanium dioxide (TiO_2) is one of the most promising materials in many industrial applications such as gas sensors, because of its high sensitivity, fast response,

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and low cost [2]. Rutile, anatase, and brookite are the three important phases in TiO_2 [3]. Anatase TiO_2 has drawn much attention, especially in renewable energy and environmental applications [4]. Because of its chemical stability, anatase TiO_2 is a significant material in gas sensing applications [5], Moreover anatase TiO_2 suffers from poor conductivity due to its wide band gap, and this usually causes increased resistance of electronic components when working. Since hydrogen is considered as a reducing gas which causes significant reduction in resistance, anatase TiO_2 is considered to be ideal semiconducting material for wide use in detecting hydrogen [6]. Anukunprasert et al., has reported that the most sensitive phase for gas sensing is found to be anatase and the phase transformation from anatase to rutile can cause a drastic decrease of sensor sensitivity [7]. Al-Homoudi has also discussed the electrical response of anatase TiO_2 films for different concentrations of CO gas (20–100 ppm) in a nitrogen gas ambient [8]. The need for control in combustion process, lowering emission, and efficient use of petrol paved way for gas sensors [9]. The absorption of gas molecules on the TiO_2 semiconductor surfaces and charge redistribution between the surfaces and the absorbed molecules are involved in gas sensing mechanism which leads to change in electronic structure and conductivity [10]. Zakrzewska has reported the sensing mechanism of TiO_2-based thin film sensors obtained by the reactive sputtering [11]. Surface defects are caused by the adsorption of gas molecules on oxide surfaces. Even small concentration of defects can cause a change in structural, electronic, and optical properties by inducing charge transfer between the absorbents and the substrates.

TiO_2 films have been deposited by different methods, such as spin-on technique [12], sol–gel process [13], chemical spray pyrolysis [14,15], sputtering [16], hydrothermal technique [17], reactive pulsed laser deposition [18] and electron beam physical vapour deposition [19]. Among them spray pyrolysis is a simple method to deposit thin films because it offers a number of advantages over other deposition processes, some of the important prospects are scalability of the process, cost-effectiveness, easiness of doping, operation at moderate temperatures which opens the possibility of wide variety of substrates, control of thickness, variation of film composition along the thickness and possibility of multilayer deposition. In addition to the growth techniques, the quality of films also depends strongly on the nature of the substrate. The structure and optical absorption characteristics of TiO_2 films grown on ITO coated glass substrates were found to show significant effect due to less lattice mismatch between TiO_2 and ITO [20,21]. Hence, in the present work, thin films of TiO_2 were prepared on ITO coated glass substrate by spray pyrolysis method for four different substrate temperatures. The effect of substrate temperature on the structural, optical and gas sensing properties of the films were reported.

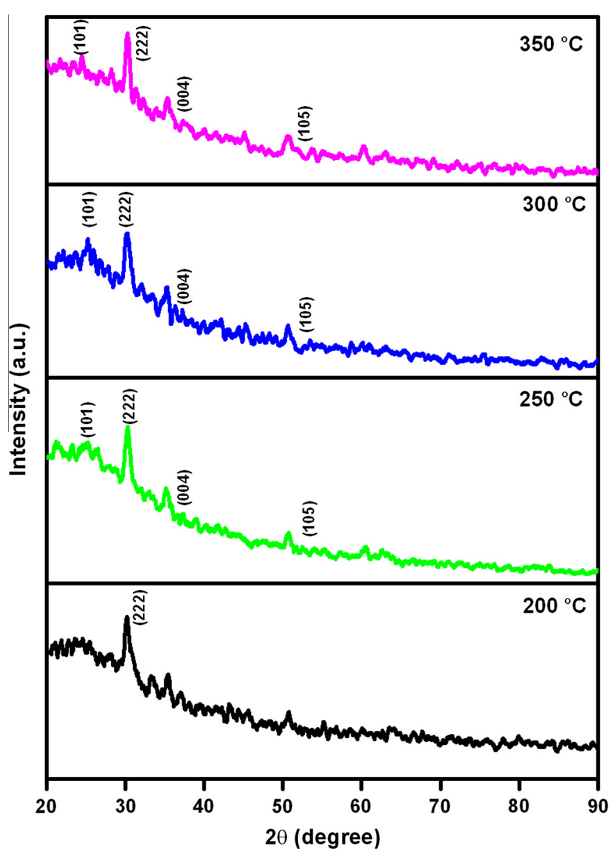

Fig. 1. XRD patterns of TiO_2 films prepared on ITO coated glass substrate at different temperatures.

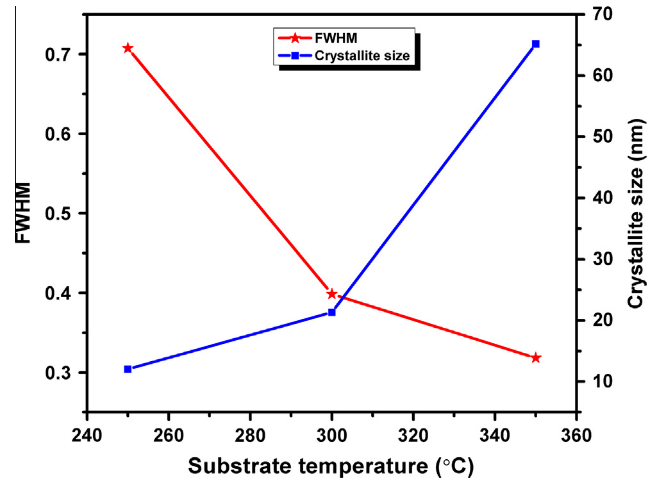

Fig. 2. Variation in crystallite size and FWHM of TiO_2 films deposited on ITO coated glass substrate at different temperatures.

Experimental procedure

The precursor solution was prepared using Titanium trichloride ($TiCl_3$) as titanium source and de-ionized water ($6H_2O$) as solvent at a concentration of 0.01 M, and stirred for 15 min. The solution was atomized by pneumatic spray system using compressed air as the carrier. Spray pyrolysis unit consists of a spraying chamber, spray gun, air compressor, temperature controller, substrate holder heater and spray nozzle. The schematic of spray pyrolysis unit used for coating thin films is discussed by the authors elsewhere [22]. To obtain good quality films, various preparation parameters like solution flow rate, nozzle to substrate distance and deposition time were optimized during deposition. ITO (222) coated glass were used as substrates, and the films were deposited using a pulsed solution feed at a flow rate of 5 ml per min. The pulses consist of 2 min spray time and 2 min pause; up to 4 pulses were used. The distance between nozzle and the substrate was 30 cm. The substrate temperature was kept at 200, 250, 300 and 350 °C for four different runs. The mixed aqueous solution is sprayed over hot substrate, which undergoes thermal decomposition, and a TiO_2 film is obtained. These films were further used to investigate the structural and optical properties. The structural characterization was done using X pert Pro X-ray diffractometer with Cu Kα radian. The optical band gap energy of the films was investigated using