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Preparation and characterization of nanocomposite TiO_2/SnO_2 films

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Abstract: This work presents the preparation of nanocomposite TiO_2/SnO_2 films by using spray pyrolysis and followed by sol-gel technique from $TiCl_4$ and $SnCl_4$ solutions. Obtained films were characterized by XRD, SEM and photoconductivity measurement. It was found that in this method the nanocomposite TiO_2/SnO_2 films were constituted of nanosized TiO_2 and SnO_2 surrounded the TiO_2 grains. The obtained nanocomposite TiO_2/SnO_2 materials were shown to have the photoconducting properties. A reason of these novel properties was discussed and practical applications of nanocomposite TiO_2/SnO_2 films were showed.

1. Introduction

TiO_2 is one of the most attracted materials in nanoscience and nanotechnology because of having a lot of interesting properties from fundamental and practical point of view [1,2,3]. Although many striking results have been achieved when using nano TiO_2 in the photo catalytic degradation of contaminated compounds or in the photo electrochemical solar-cell fabrication, efforts of scientists to improve performances of this material continuously increase day by day. In order to heighten efficiency, nano TiO_2 is usually used in the form of as either dye sensitized or nitrogen, metal doped materials. Recently a variety of mixed oxide semiconductors have been extensively studied as a new way to enhance performances of nano TiO_2 [4]. These materials could have a higher performance, even new properties. There was attempt to prepare the mixed oxide of TiO_2 and SnO_2 via a layer-by-layer technique, or by co-spray pyrolysis [5,6]. This work presents the results from preparation of TiO_2 based nanocomposite films consisted of additive SnO_2 , which is transparent conductive material [7,8], by using thermal hydrolysis techniques. As-prepared materials seem to have a photoconducting property, that could be considered as a combination between TiO_2 photosensitivity and SnO_2 conductivity.

2. Experimentals

Preparation of TiO_2 films: The principle of TiO_2 preparation in this work was based on pyrolysis of chloride salts. The starting material used in our experiments was $TiCl_4$ (99%) from

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MECRK. The salts were dissolved into distilled water to concentrations appropriate for spraying. The obtained aqueous solutions were then subjected to a spraying process with the help of a glass atomizer, operating with an air stream at 1.5 to 2 atm. The substrates were 1.2 mm-thick microscope glass slides. Substrates were preheated to a given temperature, which was kept constant with the help of an electronic digital controller. Under an open-air environment and at high temperature, hydrolysis of Ti salt solutions takes place, resulting in the formation of TiO_2 deposited on the substrate. By varying the temperatures, we found the optimal conditions for preparing TiO_2 with high performance. TiO_2 films were formed on the glass substrates at temperatures in the range of 350-450 ^oC. Such prepared films had average thicknesses from 200 to 230 nm, measured by using Alpha step equipment.

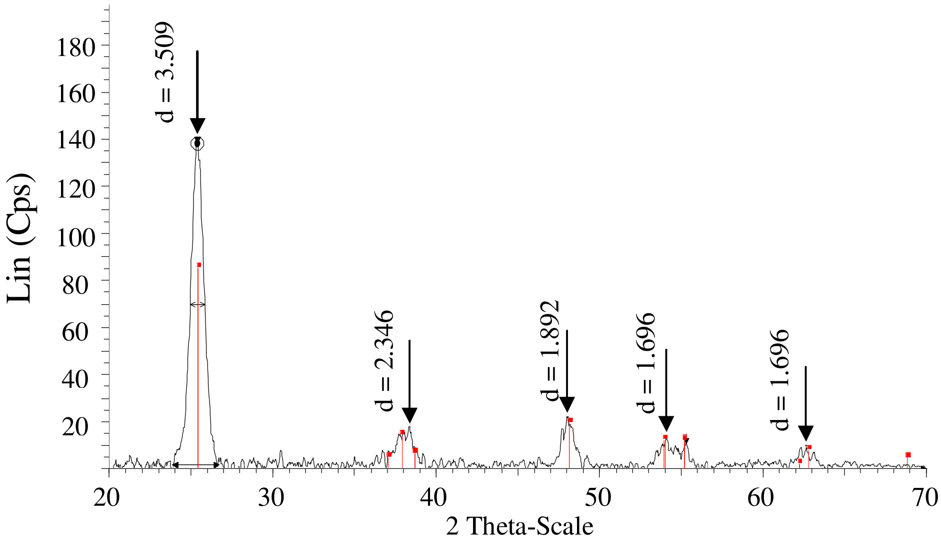

Fig. 1. XRD from TiO_2 film prepared at 400 ^OC.

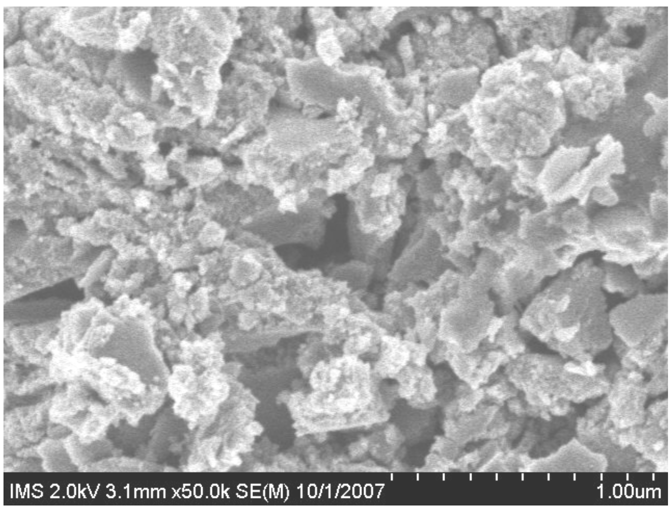

Fig. 2. The SEM of TiO_2 prepared at 400 ^oC.

After deposition, the obtained films were subjected to X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses to identify the structure, and the morphology of the samples. Figure 1 shows the XRD result for the TiO_2 film prepared from $TiCl_4$ at 400 °C. The sharp peaks of the XRD pattern indicate that TiO_2 with high crystallinity and high phase purity was formed from the $TiCl_4$ solution by using thermal hydrolysis. The average size of crystalline TiO_2 calculated from the XRD data is ca 9-15 nm. The morphology of film is shown in Fig. 2. The films prepared by using spray pyrolysis were shown to have a porous structure. The evaporation of solvents and volatile products, took place simultaneously with the deposition process, caused the porosity of the TiO_2 films.

Prepareation of TiO_2/SnO_2: After the material characterization had been determined, the obtained nano crystalline TiO_2 were subjected to the coating with SnO_2. Because of porous structure, the TiO_2 films were coated by using the sol-gel method. The films were impregnated in the sol prepared from $SnCl_4$. When the films had been dried, they were followed by annealing at high temperature in order to form SnO_2. For the best results, impregnations were carried out by varying concentration of the $SnCl_4$ solution, and the films were annealed at different temperatures and for different period of time.

Photoconductivity measurement

In order to evaluate properties of obtained films we have used the photoconductivity measurement. The samples were prepared in a shape of photo resistor. Contact electrodes were made from SnO_2:F. The sheet resistance of the contacts is about 10 Ω/□. The connections of these contacts with output terminals were realized by help of the silver paste. Contacting characteristics of the systems SnO_2:F/TiO_2/SnO_2:F was evaluated by the current-voltage measurement. The typical results are shown in Fig. 3. As is seen from Fig. 3, the contacts between SnO_2 to investigated TiO_2 are shown to be of the Ohmic, which required for photoconductivity measurement.

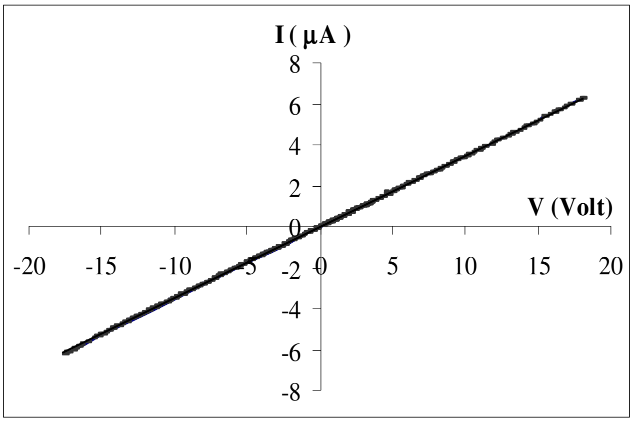

Fig. 3. I-V characteristic of SnO_2 /TiO_2:SnO_2 /SnO_2 system.

The dark resistance (R_D) and the light resistance (R_L) under the irradiation of 7W Hg lamp at the distance of 10cm were measured. The calculated ratio of R_D/R_L was considered as a photoconductivity of obtained materials. The results of measurements show that all values R_L, R_D, and R_D/R_L strongly depend on the temperature and time of annealing as presented in Fig. 4.

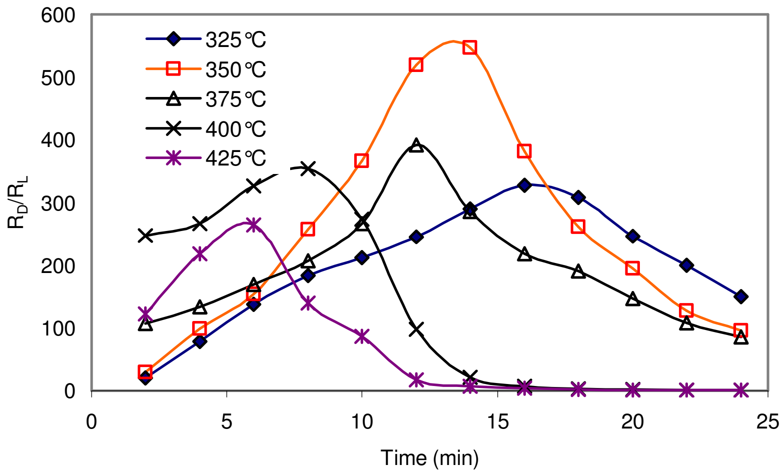

Fig. 4. The R_D/R_L dependences of TiO_2 films impregnated for 20 hours in the 0.8M $SnCl_4$ solution on the temperatures and time of annealing.

Photoconductivity spectra of these photo resistors were also estimated. Fig. 5 shows this characteristic, which was determined under visible irradiation of a Halogen lamp through the prism monochromator. It can be seen that TiO_2/SnO_2 photoresistors are sensitive only to ultraviolet rays.

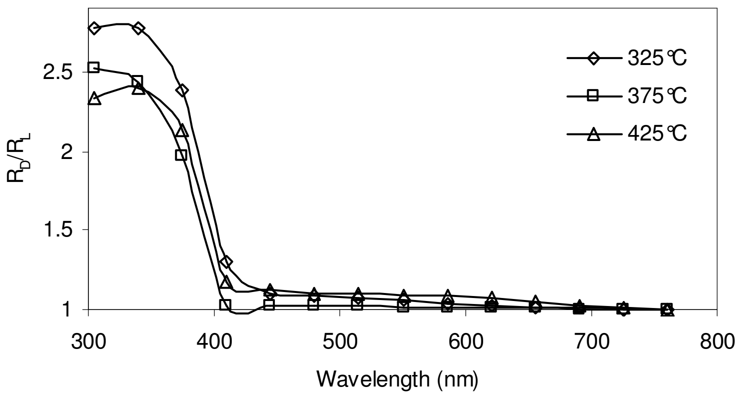

Fig. 5. R_D/R_L spectra of TiO_2 prepared at 400°C impregnated and annealed at 325, 375 and 425°C.

3. Discussion

TiO_2 belongs to dielectric materials. With a wide band gap of 3.2 eV, at room temperature there are no free carriers in the conducting band. Under ultraviolet irradiation of a wavelength shorter than the 380nm, TiO_2 can be excited, some photo electrons jumped to conducting band and can take part in the electric conduction. However the systems of high energy band gap having a tendency to produce high potential barrier on the grain boundary, impedes intergrain movement of excited carriers. Therefore there was no photocurrent appeared despite the material was irradiated. SnO_2 is the high conducting material. When deposited on the surface of TiO_2 grains they could decrease potential barriers so excited carriers can be easily to move through, produced photocurrent in this system. In this work, SnO_2 was formed from $SnCl_4$ during annealing impregnated TiO_2 film. Therefore photoeffect of impregnated TiO_2 films increases according to time and temperature of annealing. In the other hand, SnO_2 is self-doping semiconductor. Due to the stoichiometric deviation, some Sn atoms were formed and played a role of the dopant. These dopant atoms at high temperature and for a long time annealing experienced an oxidation, which resulted in the decrease of photo effect as shown in Fig. 4. The existence of two conflicting processes is the reason of the maximal photo effect during the annealing time.

4. Conclusions

The nanocomposite TiO_2/SnO_2 films have been prepared via two steps of spray pyrolysis for TiO_2 and sol-gel for SnO_2. As prepared films exhibit a nanocomposite structure, constituting of a majority of TiO_2 and a small amount of SnO_2 located on the TiO_2 grain surfaces, which decreased potential barriers, made photocurrent appear in the system under irradiation of UV light.

This result suggests a manufacture of the highly efficient UV detector by using simple methods and inexpensive materials.

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