Effect of Annealing Temperature On Iron Doped Titanium Dioxide Thin Films Prepared By Spin Coating Technique

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ABSTRACT

Iron (Fe) doped titanium dioxide (TiO_2) thin films have been successfully deposited by using spin coating technique. X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) were employed to characterize the microstructure and crystallite morphology of the films. It was indicated that the rutile crystal orientation appears due to increasing annealing temperature of the thin films. Furthermore, increasing annealing temperature of the thin films yielded an increasing of porosity value which is related to the application on gas sensor films.

Keywords: Iron doped titanium dioxide, Spin coating, Porosity value

INTRODUCTION

Titanium dioxide (TiO_2, titania) is one of the most interesting candidates for gas detection [1,2]. The sensing capability of TiO_2 depends on the concentrations of both intrinsic defects and extrinsic impurities. Many dopants have been put into TiO_2 as extrinsic impurities to improve its electronic property. Few literatures report about iron (Fe) doped TiO_2, though Fe is always present in TiO_2 as an intrinsic impurity [3]. Fe doping in TiO_2 was known increasing the dielectric constant of the TiO_2 thin films 4 and also induces a structural transformation from anatase at low Fe concentration to rutile for Fe concentrations larger than 0.32 at. % [3].

In order to investigate the applications of Fe doped TiO_2 (TiO_2:Fe), thin films are used commonly due to the advantages of easy preparation, flexibility of use, and low cost in comparison to bulk materials. Among the effective methods for the synthesis of titania films, spin coating is believed to be the best alternative method for producing titania thin films[5]. Furthermore, in this method, moderation of heating or annealing temperature was done to resolute the uncertainty concerning the suitability of anatase and rutile polymorphs for photocatalytic applications. This uncertainty lies in the contradiction between anatase which has higher value of band gap, transparency and surface area in comparison to the rutile polymorph[5]. This present work was aimed to investigate the effect of annealing temperature on the microstructure and crystallite morphology of the TiO_2:Fe thin films prepared by spin coating method.

EXPERIMENTAL

Titania (Merck, 99%) and iron oxide (Merck, 99%) were used as supplied. Precursors were prepared using TiO_2 solution of 0.5 M (390 mg of titania powder dilutes to 10 mL volume with distilled water) and Fe solution of 0.4 g/L (4 mg of iron oxide powder diluted to 10 mL). Both of these solutions were stirred continuously by magnetic stirrer at 700 rpm for 3 hours without heating. TiO_2 solution was mixed with Fe solution to yield TiO_2:Fe solution.

Spin coating was done by dropping ~ 0.2 mL of solution onto a glass substrate (13 mm × 13 mm × 1 mm, CAT. No. 7101) and a silicon substrate spun at 1370 rpm in air for 15 s. Spin coating process was followed by instantaneous heating at 150 °C for 30 min. Subsequently annealing was done using a furnace at a heating rate of about 20 °C/min and soak time of 8 hours at temperatures of 600 °C for the glass substrate and 800 °C for the silicon substrate.

The structure and the surface morphology of the TiO_2:Fe films were determined by a PAN analytical X'Pert PRO, Philips X-ray diffraction (XRD) with Cu Kα radiation (λ=1.540562 Å) and a JSM-6380LA, JEOL scanning electron microscope (SEM), respectively. Data from XRD were analyzed by using Cohen model to find out the value of lattice parameter. Meanwhile the SEM photographs were examined to investigate the grain size, homogenity and porosity of the films. The porosity of the thin films was calculated following the procedure of M. Rosi et al[6].

RESULTS AND DISCUSSION

The XRD patterns of the TiO_2:Fe thin films shown in Fig. 1 give two types of mineralogies: (1) anatase for the films annealed at 600 °C, and (2) mixed anatase and rutile for the films annealed at 800 °C.

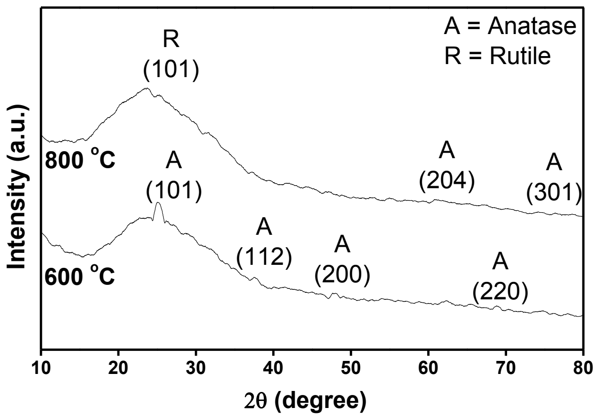


Fig. 1. X-ray diffraction (XRD) patterns of TiO_2:Fe thin films as a function of annealing temperature.

Fig. 1. shows that, the anatase to rutile transformations was occured at the annealing temperature of around 800 °C. Based on the assumption that, commonly, the anatase

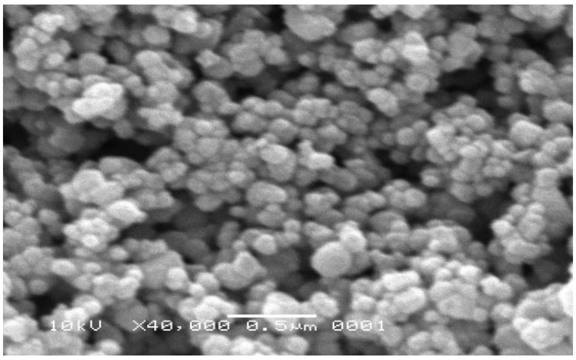
change to be rutile at ~ 600 °C, our findings indicate that the presence of dopants will increase the tranformation temperature. Or in the other words, the transformation temperature depends significantly on the presence of dopants.

Regarding to the XRD patterns, lattice parameter value and the structure of the crystal in the TiO_2:Fe thin films which has tetragonal structure could be calculated by using the Cohen method. Calculated values of the lattices parameters of the TiO_2:Fe thin films are summarised in Table 1.

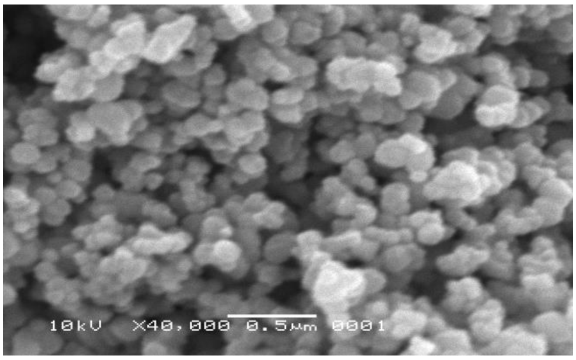
Table 1. Calculated lattice parameters of TiO_2:Fe thin films.

Annealing temperature (°C)	a=b (Ǻ)	c (Ǻ)
600	6.526	22.015
800	5.583	25.777

Table 1 shows that the crystal structure also depends on the annealing temperature. It seems that increasing annealing temperature reduces the a=b and increases the c parameter of the tetragonal crystal structure of TiO_2:Fe thin films. Furthermore, it will be related to the surface morphologies of TiO_2:Fe thin films (Fig. 2)



600 ^{o}C



800 ^{o}C

Fig. 2. Scanning electron microscope (SEM) micrographs of TiO_2:Fe thin films as a function of annealing temperature.

These SEM micrographs show that TiO_2:Fe thin films have homogeneous grain size of about 100 nm. An alteration on crystal structure occurs due to a different annealing temperatures. Moreover, porosity analyses of the SEM micrographs by M. Rosi's procedure 6 proceed porosity value for the annealing temperature of 600 °C and 800 °C are 37.7 and 39.8, respectively. It is supposed that the growth mode of film formation converts from layer or Frank-van der Merwe to be the layer plus island or Stranski-Krastanov due to increasing the annealing temperature. This transformation causes the alteration of crystal structure and porosity of the thin films.

CONCLUSION

Increasing the annealing temperature of the iron doped titanium dioxide thin films prepared by spin coating method causes changes in crystal structure and morphology of the films. Porosity value could be calculated well by M. Rosi's procedure. Our experiment results indicated that the rutile crystal orientation appears due to increasing annealing temperature of the thin films. Regarding to the application on gas sensor films increasing annealing temperature provide a superior capability due to the increasing of porosity value of TiO_2:Fe thin films.

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