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Study on the optical properties of Mn-doped TiO_2 thin films

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TiO_2 thin films have been widely investigated for solar cell [1, 2], photocatalyst [3, 4] and gas sensor [5, 6], because they have good physical and chemical properties [7, 8]. Crystalline TiO_2 film exists in three phases: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). Rutile is known to be the most stable phase. Due to its scientific and practical importance, TiO_2 rutile has been the subject of many experimental and theoretical investigations. In present, many attempts have been made to modify the physical, chemical and optical properties by mixing TiO_2 with other materials such as V [9, 10], W [11, 12], Cr [13], Sb [14], and Ce [15] oxides.

In this work we report the preparation and characterization of $TiO_2 \cdot 0.1MnO$ thin films on Si substrates. Their structures were investigated by X-ray diffraction (XRD). Optical properties of the films were examined by a photoluminescence spectrophotometer using the 320 nm and a UV-VIS spectrophotometer in the 200–1100 nm spectral range.

Tetrabutyl titanate ($Ti(OC_4H_9)_4$) was used as titanium precursor in the process of formation of TiO_2. Hydrolysis processing was performed by mixing with alcohol. Further, the solution is modified by acetic acid and water. Fig. 1 illustrates the preparation of the mixed coating solution. Manganese was introduced as nitrate because of its solubility in ethanol. Another reason for using the nitrate was that it does not give stable complexes and hence cannot prevent hydrolysis processing [16]. Acetylacetone was added in order to help the forming of the gel. The uniformly $TiO_2 \cdot xMnO$ oxide system with $x = 0.1$ molar was obtained by calcinating the coprecipitated gels at 750 °C.

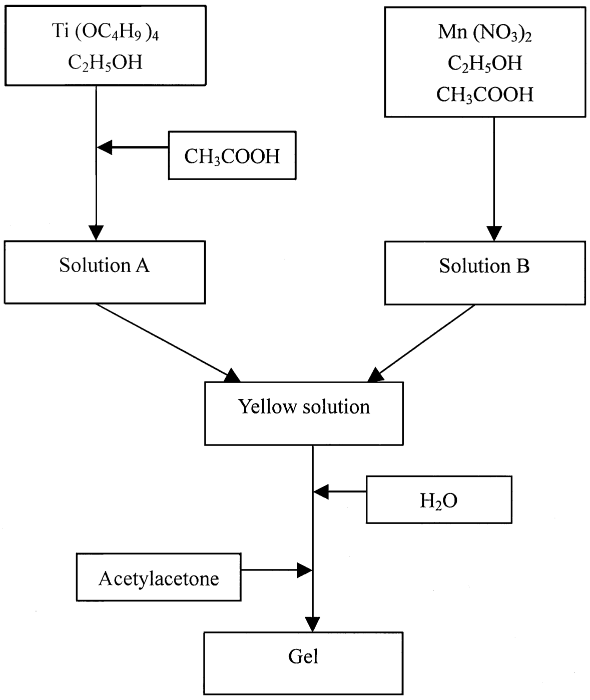

Figure 1 Preparation process of the $TiO_2 \cdot xMnO$ thin films.

Several techniques were used for characterization of the TiO_2 thin films and the $TiO_2 \cdot 0.1MnO$ thin films. The XRD was measured on a Phillips APD1700 diffractometer with nickel filtered Cu K_α radiation. Photoluminescence was measured using the 320 nm line of a mercury lamp. UV-Visible spectroscopies were performed using a Perkin Elmer Lambda 20 spectrometer in the wavelength range 200–1100 nm.

Fig. 2 shows the XRD patterns of the TiO_2 thin films and the $TiO_2 \cdot 0.1MnO$ thin films. The XRD results indicated that the TiO_2 thin films calcined at 750 °C is anatase and the $TiO_2 \cdot 0.1MnO$ thin films calcined at 750 °C is rutile. Because of the small thickness the $TiO_2 \cdot 0.1MnO$ thin films, the weak peaks are not clearly distinguished and the Si (200) diffraction peak at 33 ° peak appears.

Fig. 3 shows the photoluminescence spectrum of the TiO_2 thin films and the $TiO_2 \cdot 0.1MnO$ thin films. The luminescence of both the samples is UV-visible emission with a broad spectral width. There is a gradual shift of the emission peak towards the longer wavelength region and a decrease in the peak intensity with doping Mn into TiO_2 (see Fig. 3). The shift of the emission peak towards longer wavelengths, i.e., the lower energy

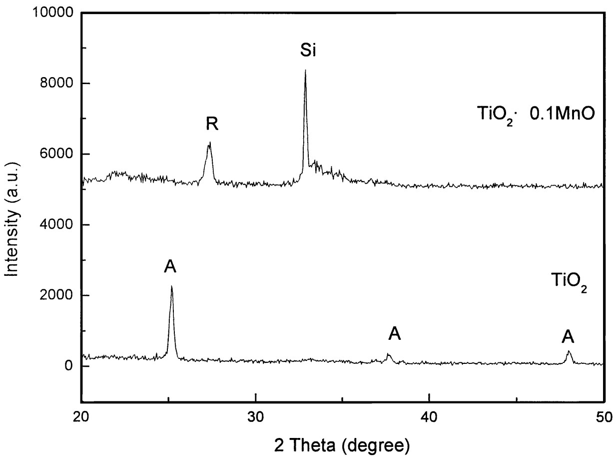

Figure 2 XRD patterns of the TiO_2 thin films and the $TiO_2 \cdot 0.1MnO$ thin films.

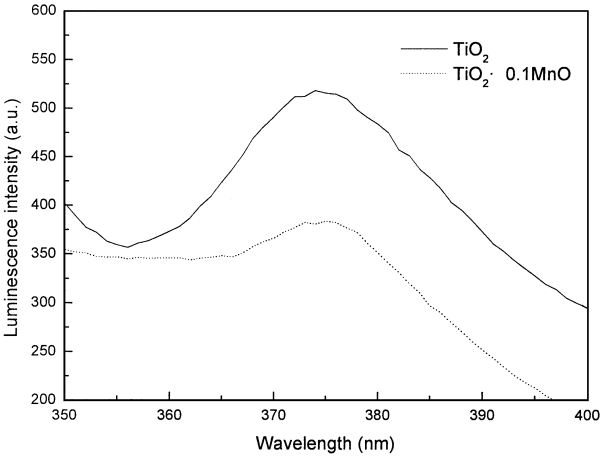

Figure 3 The photoluminescence spectrum of the TiO_2 thin films and the $TiO_2{\cdot}0.1MnO$ thin films.

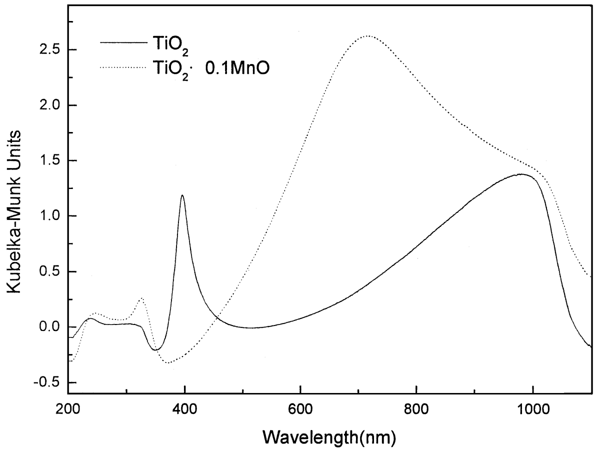

Figure 4 UV-VIS spectrum of the TiO_2 thin films and the $TiO_2{\cdot}0.1MnO$ thin films.

region, further supports the lowering of the bandgap of TiO_2 with Mn doping. The decrease in emission intensity with Mn doping may be due to the introduction of new defect sites that enhance non-radiative recombination of the excited electrons. Similar quenching in the luminescence intensity has also been observed for Pb-doped TiO_2 by Rahman [17].

Fig. 4 shows the UV-VIS spectra of the TiO_2 thin films and the $TiO_2{\cdot}0.1MnO$ thin films in wavelength range 200–1100 nm. Similar spectra were observed for both the samples. A "red shift" of the $TiO_2{\cdot}0.1MnO$ thin films could attribute to different structure and the small thickness. The differences in the film thickness should be associated to the differences in the density of the sol-gel solutions. As is known [18], usually at higher doping concentrations, the higher the density and the thinner the film.

In summary, high quality Mn-doped TiO_2 thin films with rutile phase have been successfully synthesized at 750 °C by a sol-gel method. Whereas the XRD results shows that the TiO_2 thin films calcined at 750 °C is anatase. It can be obtained from both the photoluminescence spectrum and the UV-VIS spectra that the $TiO_2{\cdot}0.1MnO$ thin films with rutile phase showed a "red shift".

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