RAMAN SCATTERING AND OPTICAL STUDIES OF Fe DOPED TiO_2 FILMS

R. Naik [1*], P. Talagala[1], G. M. Tsoi[1], V. M. Naik[2], R. Suryanarayanan[3], and G.W. Auner[4]

[2] Department of Physics and Astronomy, Wayne State University, Detroit, MI, USA;
E-Mail: naik@physics.waye.edu
[1]Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI, USA;
[3]LPCES, Université Paris-Sud, 91405 Orsay, France
[4]Department of Electrical and Computer Engineering, Wayne State University, Detroit, MI, USA

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Abstract: Anatase and rutile forms of TiO_2 and their Fe doped (5 at %) films have been made successfully using a simple spin coating metalorganic decomposition method. The Raman spectra show the characteristic modes of either Anatase or rutile TiO_2. Fe-doped TiO_2 films shows a paramagnetic behaviour both at 5 K and at room temperature.

Recently, there has been a great deal of interest in finding room temperature ferromagnetism in transparent transition metal doped TiO_2, ZnO and other materials so called diluted magnetic semiconductors (DMS) [1]. Theoretical calculations show that ferromagnetism is stable in DMS based on wide bandgap semiconductor. Hence, significant efforts have been made to grow these oxide DMS films. In the present work, we have used metalorganic decomposition (MOD), a versatile and a low cost spin coating method, for the fabrication of TiO_2 anatase and rutile forms. Rutile TiO_2 is tetragonal with a = 0.459 nm and c = 0.296 nm, and an optical bandgap of 3 eV while the anatase TiO_2 is also tetragonal with a = 0.378 nm and c = 0.952 nm with a bandgap of 3.2 eV.

Iron substituted TiO_2 films were prepared on sapphire substrates using MOD spin coating method. Separate solutions were made using different concentrations of Ti-ethylhexoxide, and Fe-ethylhexanoate precursor solutions. Films (thickness ~1μm) were prepared by dispensing the metalorganic solution onto substrates. The Raman spectra were recorded using a single monochromator (Instruments SA-Triax 550), using a 514.5 nm excitation line in a nearly back-scattering geometry. Optical transmission spectra were recorded in the 190-1000 nm range using a UV/Visible spectrometer. Magnetic measurements (M vs H curves at different T) were made using a SQUID magnetometer.

The films annealed at 550 ^oC show only anatase phase, whereas the films annealed at 700 ^oC show only rutile pahse as confirmed by x-ray diffraction patterns (not shown here). Figure 1 shows the corresponding Raman spectra of anatase and rutile forms of TiO_2, and Fe-doped (5 at%) TiO_2 films. The characteristic phonon modes expected for the anatase and rutile forms are observed. These are in full agreement with the spectra observed in single crystalline forms rutile and anatase-TiO_2 both of which belong to D_{4h} space group [2,3]. The broad band ~235 cm^{-1} in R- TiO_2 has been assigned as a combination line rather than a fundamental one phonon process [3]. The 612 cm^{-1} (A_{2g}) phonon region also has combination bands in the vicinity making the room temperature A_{2g} mode broad and asymmetric.

The Raman spectra of anatase and rutile forms clearly show that the crystal structure of TiO_2 remains unaltered upon Fe-substitution, and there is no indication of the Fe oxide formation. Similarly, the optical absorption spectra (Fig. 2) also remain almost unaffected upon Fe-substitution indicating that Fe may have occupied the substitutional sites in the TiO_2 host lattice.

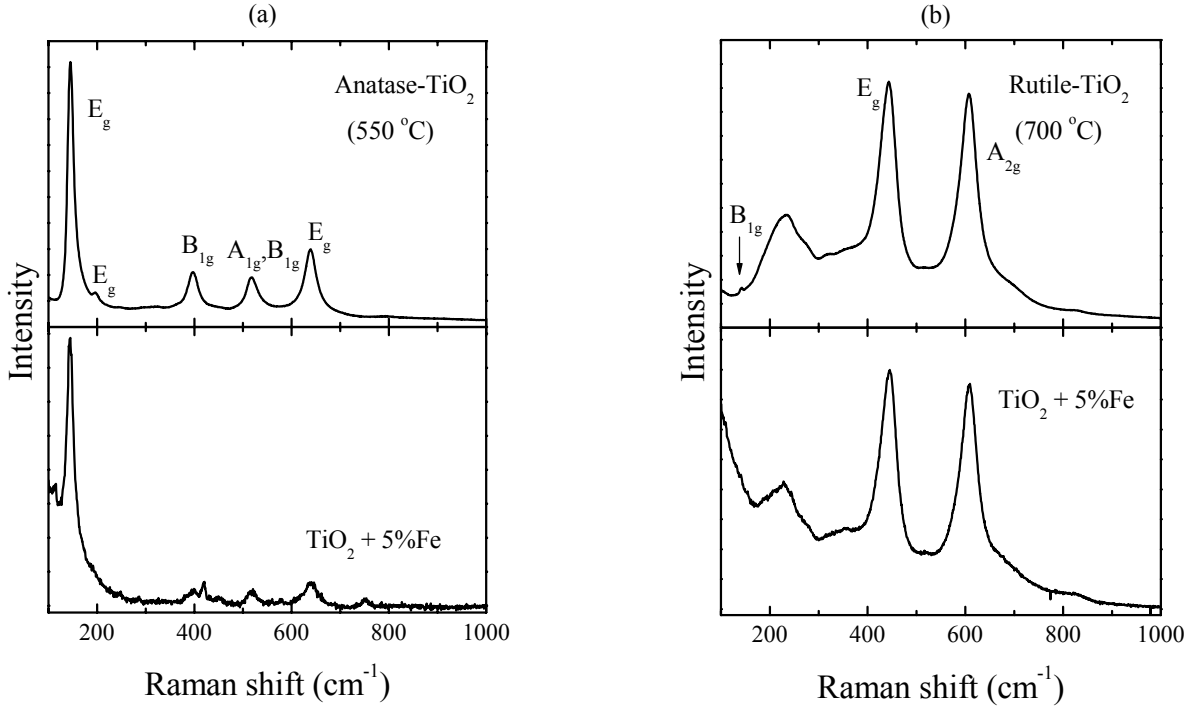

Fig. 1. Raman spectra of (a) anatase and (b) rutile TiO_2, and Fe-substituted TiO_2 films. The annealing temperature is also shown above.

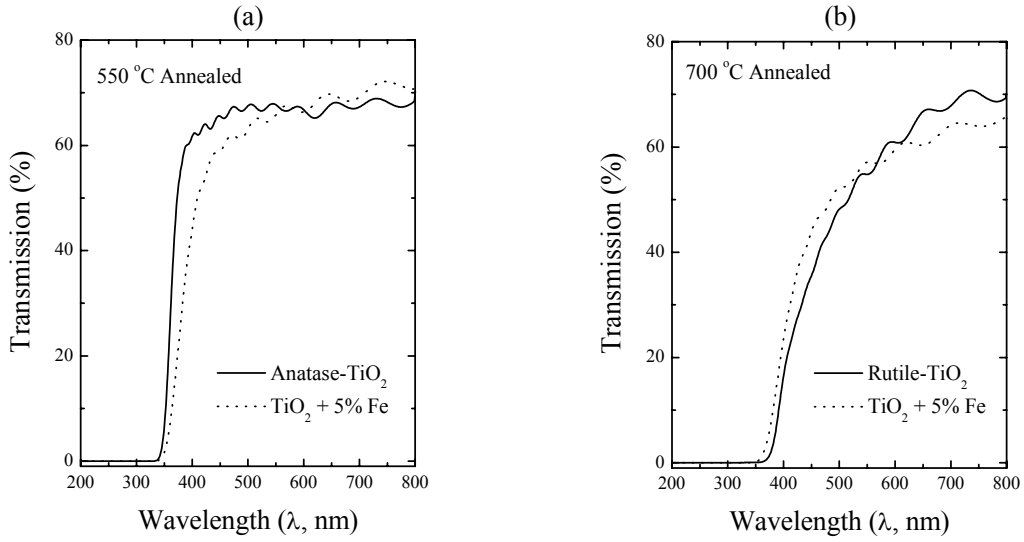

Fig. 2. Optical absorption spectra of (a) anatase and (b) rutile TiO_2, and Fe-substituted TiO_2 films.

The Magnetization versus magnetic field data (figures not shown here) measured using a SQUID magnetometer show that the Fe-doped TiO_2 films are paramagnetic both at 5 K and at room temperature.

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