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Article

Composition Dependence of Microstructure, Phonon Modes, and Optical Properties in Rutile TiO_2:Fe Nanocrystalline Films Prepared by a Nonhydrolytic Sol–Gel Route

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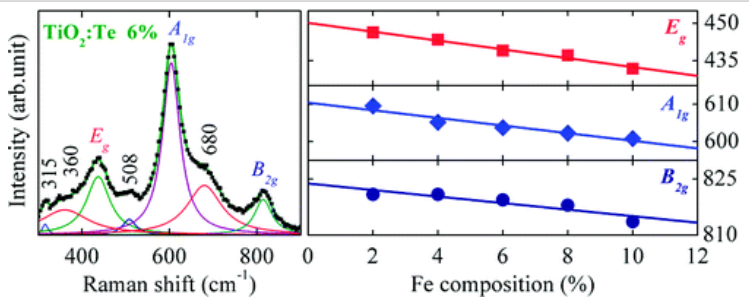
Section: Optical, Electron, and Mass Spectroscopy and Other Related Properties

Abstract



Iron-doped titanium dioxide nanocrystalline (*nc*-TiO_2:Fe) films with the a composition from 2 to 10% have been deposited on Si(100) substrates by a facile nonhydrolytic sol–gel route. X-ray diffraction analysis shows that the films are polycrystalline and exhibit the pure tetragonal rutile phase structure. The Fe dopant effects on the surface morphology, microstructure, phonon modes, and dielectric functions of the *nc*-TiO_2:Fe films have been investigated by atomic force microscopy, ultraviolet Raman scattering, far-infrared reflectance, and spectroscopic ellipsometry at room temperature. With increasing Fe composition, the first-order Raman-active phonon modes E_g, A_{1g}, and B_{2g} are shifted toward a lower frequency side of 10, 6, and 7 cm^{-1}, respectively. The four additional vibrations, which are strongly related to the surface structure of the films, can be observed due to the two-phonon scattering process. Moreover, the three infrared-active transverse-optic (TO) phonon modes E_u (TO) can be located at about 183, 382, and 500 cm^{-1}, respectively. The dielectric functions of the films have been uniquely extracted by fitting the measured ellipsometric spectra with a four-phase layered model (air/surface rough layer/film/Si) in the photon energy range 0.73–4 eV (310–1700 nm). Adachi's dielectric function model has been successfully applied and reasonably describes the optical response behavior of the *nc*-TiO_2:Fe films from the near-infrared to ultraviolet photon energy region. It is found that the real part of dielectric functions in the transparent region slightly decreases with increasing Fe composition.

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Furthermore, the optical band gap linearly decreases from 3.43 to 3.39 eV with increasing Fe composition due to the energy level of Fe t_{2g}, which is closer to the valence band. It is believed that the decrease of the optical constants and optical band gap for the *nc*-TiO_2:Fe films with the Fe composition is mainly ascribed to the differences of the crystallinity and the electronic band structure, which can be perturbed by the transition metal introduction.

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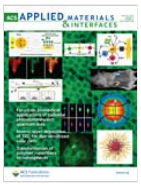

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