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Lattice Vibration Fundamentals of Anatase Nanocrystalline TiO_2 Thin Films Detected Using Unpolarized Infrared Spectroscopy

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Unpolarized infrared spectroscopic study was carried out on thin nanocrystalline anatase TiO_2 films with grain size of $\approx$20 nm. The transverse optical lattice vibration frequencies are the same as that of single-crystal anatase. The longitudinal optical modes can be detected with an oblique unpolariation at incident angles $\geq 50°$. The broad LO absorption peak is a combination of the A_{2u} LO and the E_u LO modes' resonant response to the infrared radiation.

In a single crystal, long wavelength lattice vibration modes are associated with atomic motion perpendicular and parallel to the direction of lattice wave propagation, which are denoted as transverse optical (TO) and longitudinal optical (LO) modes. In general, polar LO phonons do not couple to a transverse probing wave in a first-order infrared-absorption process. The LO phonon frequencies, ω_{LO}, are therefore usually obtained by using the Lyddane–Sachs–Teller relationship, $\omega_{LO} = \omega_{TO}(\varepsilon_0/\varepsilon_\infty)^{1/2}$, where ω_{TO}, ε_0, and ε_∞ are the TO phonon frequency, dielectric constants at very low and very high frequencies, respectively.[1] A second method to obtain ω_{LO} is to fit the observed reststrahlen reflectance curve using a dielectric dispersion relation in which ω_{LO} is a variable parameter. Usually, polarization-dependent infrared reflectivity of a single crystal is measured and then the reflectivity curve is fitted using a factorized form of dielectric function to obtain the phonon frequences.[2] However, both of these two methods have difficulties or lacks accuracy because of the difficulty of obtaining single crystals for some materials or the uncertainty as to the values of ε_0 and ε_∞. As mentioned above, polar LO phonons do not couple to a transverse probing wave in a first-order infrared-absorption process. However, this rule may be relaxed in such circumstances as in disordered system, multiphonon processes, and small-sized samples, specifically in thin films whose thickness is far shorter than the infrared wavelength.[3] In such systems, an oblique incident *p*-polarization component of an infrared radiation is required to observe the LO or LO-like mode features.[3–5]

Titanium dioxide TiO_2 is one of the most investigated transition-metal oxide materials owing to its wide application possibilities. TiO_2 can be used in the fields of optical filters, optical waveguides, chemical sensors, solar cells, and more.[6–8] The lattice fundamentals and optical properties of single crystal TiO_2 have been studied by both experimental and theoretical mothods.[3,9] Recently, vitreous TiO_2 thin films with anatase atomic short-range order (SRO) were studied by polarization-dependent infrared spectroscopy.[4] In this letter, we report the infrared spectroscopic study of anatase nanocrystalline TiO_2 thin films with unpolarized infrared radiation. The nanocrystalline TiO_2 represents a structure characteristic between single crystal and vitreous TiO_2 film. It is thus interesting to compare the lattice fundamentals in these three different TiO_2 forms.

The anatase nanocrystalline TiO_2 thin films were prepared by the sol–gel process. Titanium butoxide ($Ti(OC_4H_9)_4$), acetic acid, water, and absolute ethanol were used as the reaction precursors. Polyethyleneglycol 400 was added as the complexing agent into the formed sols. The gels prepared could be stable up for several months, which allowed us to obtain very homogeneous thin films with large area size. The thin films were deposited by spin coating using a standard photoresist spinner. The nanocrystalline thin films were obtained by heating the spinned gels up to 450 °C for 30 min. The substrates used were glass plates coated with conducting indium tin oxide or (001) silicon wafers. Film thicknesses ranged from 100 to 1000 nm. The deviations of the film thickness and refractive index of a $2 \times 2\,cm^2$ film were within 5%, which were mapped out using an automatic ellipsometer.

Figure 1a shows the atomic-force microscopy (AFM) surface topography of a 300-nm-thick TiO_2 film. It can be seen that the film is composed of nanosized grains ($\approx$20 nm) with a very homogeneous grain size. Such a grain size is the most desirable one for the dye-sensitized solar cell.[8] Figure 1b shows the X-ray diffraction (XRD) data, which show only the anatase peaks; no rutile peaks were observed after the heat treatment at 450 °C. The wide peak under the (101) peak comes from the glass substrate. The strong (101) peak indicates that the anatase film preferably crystallized with (101) planes parallel to the substrate. The full width at half maximum (FWHM) of the (101) peak is used to calculate the coherence depth, which is given by the Scherrer formula. The coherence depth calculated is 17 nm, which is about 3 nm smaller than that measured by the AFM image. However, considering a possible AFM tip artifact, which usually gives a somewhat larger grain size, the crystallite and grain sizes measured by these two methods are almost the same. The space group of tetragonal anatase is $I4_1/amd$, and

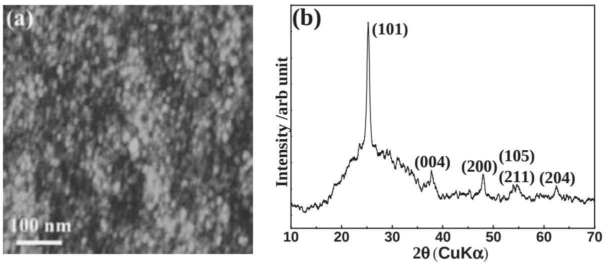

Figure 1. (a) AFM image and (b) XRD of the 300-nm-thick TiO_2 film.

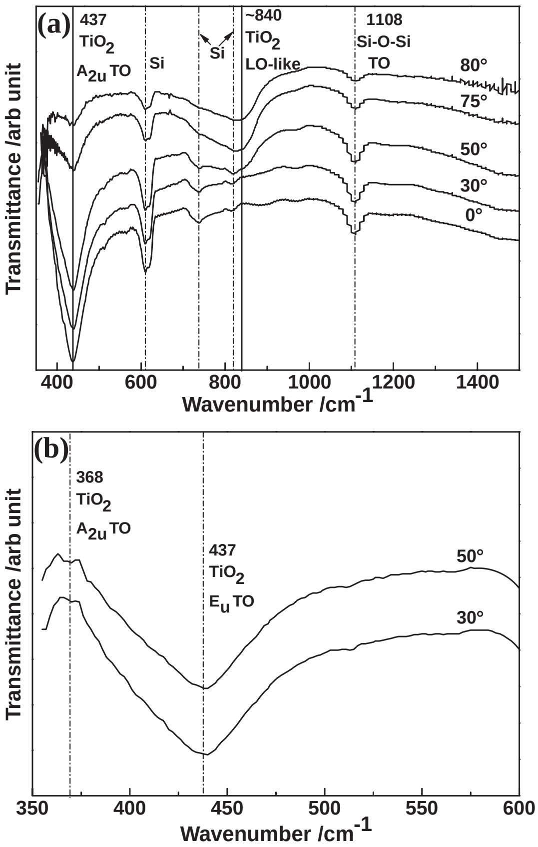

Figure 2. (a) Angle-dependent unpolarized infrared spectra of the 300-nm-thick TiO_2 film; (b) spectra in the wave number range of 350–600 cm^{-1} to show the A_{2u} TO mode more clearly.

the local symmetry is D_{2d}. In the primitive cell, there are two TiO_2 units, giving six Raman-active fundamentals in the vibrational spectrum: three E_g, two B_{1g}, and one A_{1g} modes, which were all observed in our thin anatase films, and no rutile Raman peaks were observed. This again confirms the pure anatase phase observed by the XRD. The strongest Raman peak of E_g locates at 145 cm^{-1} with a FWHM of 15 cm^{-1}. A correlation between Raman frequency and peak width has been established as a characteristic feature of the Raman spectra of nanocrystalline TiO_2, and spatial confinement of phonons in nanosized crystals is the major factor determining the Raman spectral characteristics.[10] The relatively narrow Raman peak width for the 20-nm-sized grain TiO_2 film, compared with published data,[10] shows that our TiO_2 films is composed of nanocrystalline grains with a narrow grain-size distribution (as can also be seen in Figure 1a) and within each individual nanocrystalline grain, the atoms are well ordered in the anatase phase.

The angle-dependent infrared spectra of the 300-nm-thick TiO_2 film with unpolarized radiation are shown in Figure 2. The angle values are the ones between the incident radiation and the normal of the film surface. All the absorption bands observed are labeled in the figure. For anatase structure, three modes are infrared active, the A_{2u} mode and the two E_u modes. The A_{2u} mode is active for light polarized parallel to the *c* axis; while the E_u modes are active for light polarized perpendicular to the *c* axis. All the spectra show two TO modes, namely A_{2u} TO and E_u TO at 368 and 437 cm^{-1}, which are more clearly shown in Figure 2b. It is interesting to note that these two TO values are almost the same as that of single-crystal anatase, which has values of 367 and 435 cm^{-1}, respectively.[2] When the radiation angle increases to 50°, a broad LO-like absorption peak appears at $\approx$740 to 900 cm^{-1}, and the peak moves to a larger wave number when the incident angle increases. For a single crystal, the LO loss function, defined as the imaginary part of the negative inverse dielectric function, has a peak at an LO mode resonance. For randomly oriented Ti–O units, unlike the TO loss function, the LO loss function is significantly different from those of single-crystal anatase.[4] For such a system with a granular nanostructure, the dielectric function can be described by a simple directional average of the dielectric functions of a single crystal: $\varepsilon(\nu) = [2\varepsilon_{\perp}(\nu) + \varepsilon_{\parallel}(\nu)]/3$, where $\varepsilon_{\perp}(\nu)$ and $\varepsilon_{\parallel}(\nu)$ are the dielectric functions for the $E \perp c$ and $E \parallel c$ orientations, and E and *c* are the applied electric field and the *c* crystallographic vector, respectively.[4,11] Therefore, under unpolarized radiation, the LO loss function is a linear combination of the dielectric functions corresponding to A_{2u} LO and E_u LO modes. The observed broad LO-like peak is at $\approx$840 cm^{-1}, which lies between the single-crystal A_{2u} LO and E_u LO modes, whose values locate at 755 and 876 cm^{-1} for $E \parallel c$ and $E \perp c$ configurations, respectively.

The infrared spectroscopic study of nanocrystalline anatase clearly shows that the TO lattice vibration frequencies are completely the same as that of single-crystal anatase. The LO modes can be detected with an oblique unpolarized radiation at angles $\geq$50°. The broad LO infrared absorption peak is a combination of A_{2u} LO and E_u LO modes resonance response to the infrared radiation.

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