

Raman spectroscopy study of the phase transformation on nanocrystalline titania films prepared via metal organic vapour deposition

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Abstract Raman spectroscopy (RS) was used to study the phase transformations of nanocrystalline TiO₂ thin films. The films were grown by a vertical-flow cold-wall metal organic chemical vapour deposition system, using Ti(C₁₀H₁₄O₅) as the source reagent, at different substrate temperatures. The results indicate that the anatase phase is present at around 550 °C and the rutile phase starts to form at 620 °C. The anatase phase completely transforms into the rutile phase at 680 °C. We have demonstrated that RS can be used as a powerful nondestructive technique for a quick and efficient determination of the phase of TiO₂ thin films.

1 Introduction

Titania (TiO₂) has been widely studied because of its unique optical and chemical properties in catalysis [1], photocatalysis [2], and nonlinear optics [3]. The material crystallizes mainly in anatase or rutile phase and exhibits different physical and chemical properties. It is well-known that the anatase phase is suitable for catalysts and supports

[4], while the rutile phase is used for optical and electronic purposes because of its high dielectric constant and high refractive index [5]. Although at ambient pressure and temperature the rutile phase is more thermodynamically stable than the anatase phase [6], the latter is the common phase for the formation of nanocrystalline TiO₂ at relatively lower temperature because it is kinetically more stable than the rutile phase [7]. It has been reported that the anatase phase transforms to the rutile phase at some higher temperatures. However, the temperature of phase transition may vary according to the methods of synthesis. Therefore, understanding and controlling of the crystalline phase and the process of phase transformation of TiO₂ are important.

Raman spectroscopy (RS) is an important nondestructive structural characterization tool that can be used to investigate amorphous to crystalline phase transitions, oxygen defects, stress states and quantum size effects in transition metal oxides [8, 9]. This non-invasive method offers quantitative microanalysis without damaging the sample which is the trend for electronic materials characterization. In the case of TiO₂, Raman spectroscopy can identify its naturally occurring crystalline phases such as anatase, rutile and brookite [10].

In this study, we report the investigation of structural transformations in nanocrystalline TiO₂ thin films by Raman spectroscopy. The films were grown by a vertical-flow cold-wall metal-organic chemical vapour deposition (MOCVD) system on sapphire (SA)(100) substrates, using titanium (IV) oxide bis(acetylacetonate) [Ti(C₁₀H₁₄O₅)], as the source reagent, at different substrate temperatures. Combined with X-ray diffraction (XRD), RS is used to extract the structure and phase information of the as-deposited TiO₂ films. The usefulness of RS as a nondestructive phase transformation characterization technique for nanostructural TiO₂ thin films will be demonstrated.

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2 Experimental details

A vertical-flow cold wall MOCVD system was utilized for the growth of the samples on sapphire(100) substrates. The titanium (IV) oxide bis(acetylacetonate) as the source reagent supplied by Strem Chemicals was used for chemical vapor deposition of nanostructural TiO₂ films. High purity argon and oxygen were used as the carrier and reactive gas with flow rate fixed at 300 and 200 sccm, respectively. The argon flow carried the metalorganic vapor through the precursor reservoir and the heated transport line, which were maintained at 170 °C to prevent vapor condensation during the transportation. The oxygen passed through a gas ring set above the substrate and reactive with the vapor came out from the shower head. The chamber pressure was kept at 3 mbar. The temperature of the substrates, T_s, was set between 550 and 680 °C for different targeted growth.

The morphology of the as-deposited samples was studied with a JEOL-JSM6500F field-emission scanning electron microscopy. X-ray diffraction patterns taken on a Rigaku RTP300RC X-ray diffractometer equipped with a Cu K_α radiation source and a Ni filter were used to examine the crystallographic characteristics of the samples over a large area of the surface. Raman spectroscopy was used to extract the phase information of the TiO₂ films. Raman spectra were recorded at room temperature utilizing the backscattering mode on a Renishaw inVia micro-Raman system with 1,800 grooves/mm grating and an optical microscope with a 50× objective. The Ar-ion laser beam of the 514.5 nm excitation line with a power of ~1.5 mW was focused into a spot size ~5 μm in diameter. Prior to the measurement, the system was calibrated by means of the 520 cm⁻¹ Raman peak of a polycrystalline Si.

3 Results and discussion

3.1 Lattice dynamics of anatase and rutile phases in TiO₂

Titania crystallizes mainly in anatase or rutile phase. Anatase is tetragonal and belongs to the space group D_{4h}^{19} [11]. The primitive unit cell contains two TiO₂ chemical units. According to the factor group analysis, there are six Raman active modes ($1A_{1g} + 2B_{1g} + 3E_g$) [12]. The Raman spectrum for anatase single crystal was investigated by Ohsaka et al. [13] and six allowed bands in the first-order Raman spectrum were identified at 144 cm⁻¹ (E_g), 197 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 516 cm⁻¹ ($A_{1g} + B_{1g}$), and 639 cm⁻¹ (E_g). The Raman band occurring at 516 cm⁻¹ at room temperature is split into two peaks centred at 513 cm⁻¹ (A_{1g})

and 519 cm⁻¹ (B_{1g}) at 73 K [13]. Rutile is also tetragonal and belongs to the space group D_{4h}^{14} with two TiO₂ molecules per unit cell. There are four Raman active modes with symmetry of A_{1g} , B_{1g} , B_{2g} , and E_g [12]. These four Raman-active modes of rutile TiO₂ were detected at 143 cm⁻¹ (B_{1g}), 447 cm⁻¹ (E_g), 612 cm⁻¹ (A_{1g}), and 826 cm⁻¹ (B_{2g}) by Porto et al. [14]. Furthermore, the Raman spectra of anatase exhibit features different from those of rutile: second-order scattering in rutile is even more intense than one-phonon scattering, whereas in anatase only a few weak bands due to two-phonon scattering are observed.

3.2 Evolution of anatase phase in nanocrystalline TiO₂

Figure 1 depicts the Raman spectra for the nanocrystalline TiO₂ films deposited at (a) 550 °C, (b) 600 °C, and (c) 620 °C. As shown in curve 1(a), the S/N ratio of the Raman spectrum of TiO₂ film deposited at 550 °C is rather large. This might be due to the low temperature of deposition which can result in thin and low film crystallinity. In addition to the substrate peaks indexed by S, a weak Raman peak at 152 cm⁻¹ and three broader features in the high-wavenumber region located at around 405, 519 and 643 cm⁻¹ are also detected. The Raman features observed in the spectra are close to those in the bulk anatase phase, except for their lower intensity and broader linewidth. Therefore, it is evident that the nanocrystalline TiO₂ film possesses a certain degree of long-range order of the anatase phase. However, the weak overlapped broader peaks in the high wavenumber region indicate that the short-range order is poor and optical phonons may decay at the imperfect sites. Curve 1(b) is the Raman spectrum of the TiO₂ film deposited at 600 °C. One significant observation

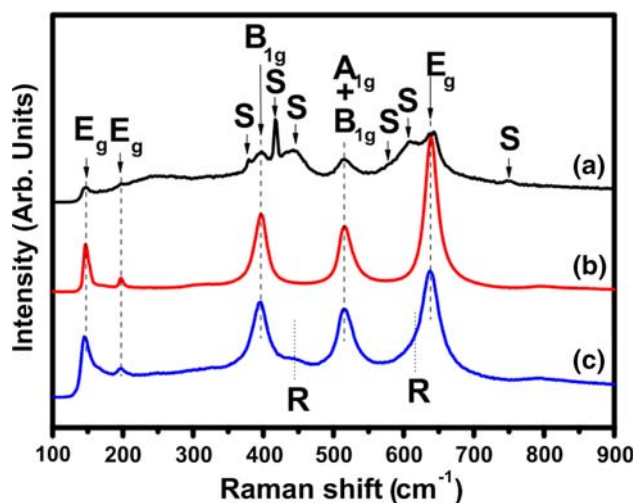


Fig. 1 Raman spectra for the nanocrystalline TiO₂ films deposited at (a) 550 °C, (b) 600 °C, and (c) 620 °C. Raman modes of rutile phase are denoted by R

of the spectrum is the intensification of the lowest wavenumber E_g mode. A very weak peak at around 196 cm^{-1} emerges at the higher wavenumber side of the E_g mode, which can also be assigned as the E_g mode of anatase

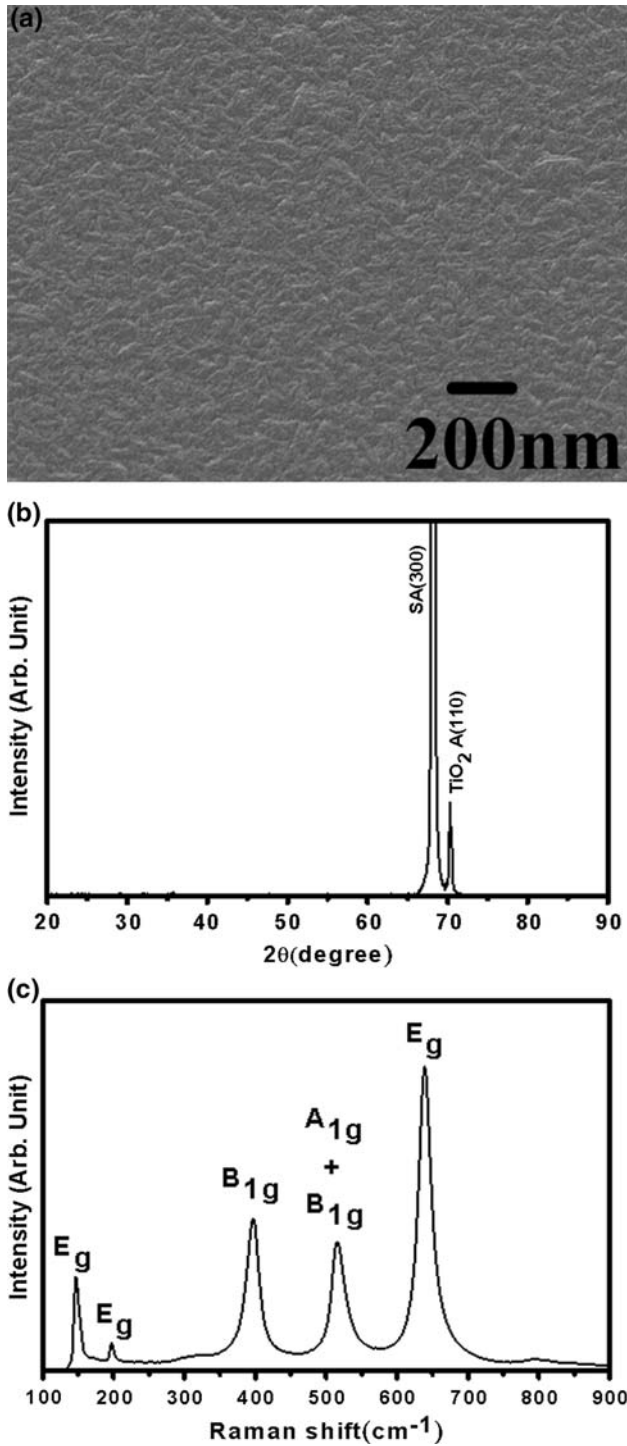


Fig. 2 (a) FESEM image, (b) XRD pattern and (c) Raman spectrum of anatase phase nanocrystalline film TiO_2 grown on SA(100) substrate at $680\text{ }^\circ\text{C}$. The XRD pattern shows the uniquely single-directional growth of anatase phase TiO_2 films along [110]

phase. The $398, 516,$ and 638 cm^{-1} features are the Raman modes in anatase phase. With the increase in substrate temperature ($550\text{--}600\text{ }^\circ\text{C}$), linewidths of the high wavenumber modes decrease and their intensities increase, indicating the enhancement of short-range order. As shown in curve 1(c), at substrate temperature increases to $620\text{ }^\circ\text{C}$, a small peak at around 448 cm^{-1} and a weak shoulder at around 608 cm^{-1} appeared. The features at 448 and 608 cm^{-1} are the E_g mode and A_{1g} mode of the rutile phase, respectively. The presence of rutile Raman modes indicates that the high-temperature rutile phase starts to form at $T_s = 620\text{ }^\circ\text{C}$.

The formation of pure anatase phase of nanocrystalline TiO_2 film at $T_s = 600\text{ }^\circ\text{C}$ is further confirmed by FESEM and XRD measurements. Figure 2(a–c) show the FESEM image, XRD pattern and Raman spectrum of the nanocrystalline TiO_2 film grown on SA(100) substrate at $600\text{ }^\circ\text{C}$. The FESEM image reveals the formation of nanosized rough surface of the film. The XRD pattern shows the preferable orientation of [110] ($2\theta \sim 70.4^\circ$) with anatase phase for the film grown on SA(100). The XRD and RS results indicate that the A- TiO_2 NCs are (110) oriented on SA(100).

3.3 Anatase to rutile phase transformations

Figure 3 depicts the Raman spectra of the nanocrystalline TiO_2 films deposited at (a) $620\text{ }^\circ\text{C}$, (b) $650\text{ }^\circ\text{C}$, and (c) $680\text{ }^\circ\text{C}$. The spectra in Fig. 3 show the strong anatase E_g mode at 150 cm^{-1} begins to weaken when the rutile modes at around 448 and 608 cm^{-1} intensify with the increase in substrate temperatures. The event of anatase to rutile transformation is clearly illustrated by curve 3(b). As can

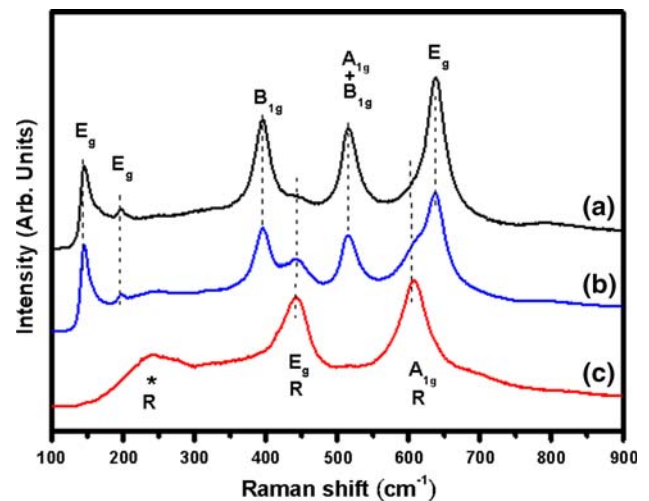


Fig. 3 Raman spectra of the nanocrystalline TiO_2 films deposited at (a) $620\text{ }^\circ\text{C}$, (b) $650\text{ }^\circ\text{C}$, and (c) $680\text{ }^\circ\text{C}$. Raman modes of rutile phase are denoted by R

be seen in curve 3(c), the anatase features disappear and the broad rutile peaks stand out in the Raman spectrum of the sample deposited at 680 °C. Curve 3(c) show that the E_g and A_{1g} modes as well as the two-phonon bands at $\sim 242\text{ cm}^{-1}$ (marked as *) are the major features of rutile TiO_2 film. The B_{2g} mode is extremely weak and B_{1g} mode is almost absent.

The formation of pure rutile phase of nanocrystalline TiO_2 film at $T_s = 680\text{ °C}$ is further confirmed by FESEM and XRD measurements. Figure 4(a–c) show the FESEM images, the XRD pattern and Raman spectrum of the nanocrystalline TiO_2 film grown on SA(100) substrate at 680 °C. The FESEM images reveal the formation of nanosized rough surface of the film. The XRD pattern shows the uniquely single-directional growth of rutile

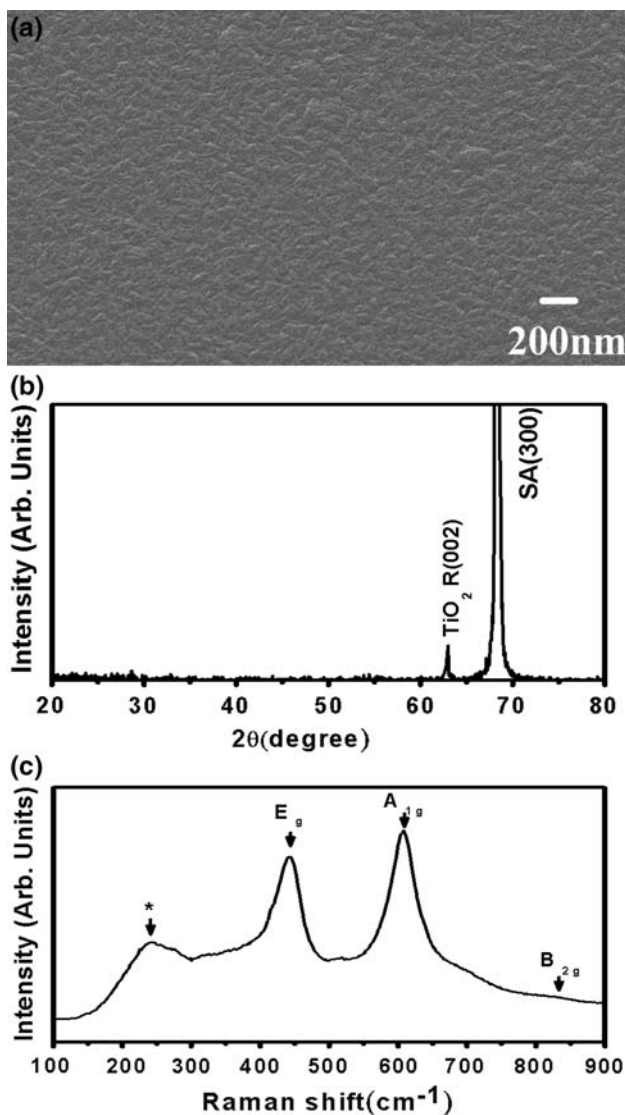


Fig. 4 (a) FESEM images, (b) XRD pattern and (c) Raman spectrum of rutile phase nanocrystalline film TiO_2 grown on SA(100) substrate at 680 °C. The XRD pattern shows the uniquely single-directional growth of rutile phase TiO_2 films along [001]

phase TiO_2 films along [001] for the film grown on SA(100). The single-directional growth of rutile phase TiO_2 films along [001] on SA(100) can be explained as the combined effects of the minimization of the oxide sublattice structural mismatch and the c -directional growth mechanism [15]. The redshifts of peak positions and broadening of linewidths of the rutile TiO_2 Raman features have been determined to be related to the phonon-confinement effect in the nanosized film and residual stress effects [16].

4 Summary

Raman spectroscopy can sensitively identify the anatase and rutile phases of TiO_2 on the basis of their characteristic Raman bands. RS was used to study the phase transformations of nanocrystalline TiO_2 thin films deposited by MOCVD. The results indicate that the anatase phase is present at around 550 °C and perfect anatase phase is formed at a temperature of 600 °C. The rutile phase starts to form at 620 °C, and the anatase phase completely transforms into the rutile phase at 680 °C. These results are further confirmed by X-ray diffraction. We have demonstrated that RS can be used as a powerful nondestructive technique for a quick and efficient determination of the phase of nanostructural TiO_2 .

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