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Letter

# Brookite-rich titania films made by pulsed laser deposition

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**Abstract**

Pulsed laser deposition has been used to prepare thin films of $TiO_2$ on silicon and other substrates. X-ray diffraction and Raman scattering results show that brookite is the main phase present in the films. Brookite has not previously been reported for pulsed laser deposited titania thin films. © 2000 Published by Elsevier Science S.A. All rights reserved.

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Titania, $TiO_2$, exhibits three crystal phases as naturally occurring minerals: rutile, anatase, and brookite. $TiO_6$ octahedra are interconnected differently for each phase, leading to different structures and symmetries. To the natural polymorphs are added two high-pressure phases which have been synthesized by shock-wave compression of rutile [1]. Amorphous titania [2,3] and brookite [4] have also been synthesized, using sol-gel techniques. In nature, rutile is the most common crystal phase and brookite is the rarest.

Various optical applications have been proposed for titania thin films because of their high refractive index and stability [5]. Transparency in the visible and absorption in the ultraviolet make them candidates for filters [6]. Other potential applications for $TiO_2$ films are as electrodes in photochemical solar cells [7] and as dielectrics in thin film capacitors [8,9]. Rutile is usually the dominant phase in $TiO_2$ films [5,8,9], but in some recent work anatase-rich films have been synthesized [8–13]. One recent paper reports $TiO_2$ films containing anatase and rutile/$TiO_2$ II phases [14]. Brookite is the most difficult titania phase to prepare in thin-film form [8,9]: Brookite-containing films have been reported for vapor-deposited films [15] (an early report not reproduced elsewhere) and films obtained by the electrochemical oxidation of titanium electrodes [11,12].

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In this letter, we report the preparation and structural characterization of $TiO_2$ films synthesized by pulsed laser deposition (PLD). Previous studies of PLD titania have reported films found to be amorphous [16] or containing rutile and anatase and off-stoichiometry phases [13]. In the present work, we have synthesized PLD polycrystalline films composed primarily of brookite and anatase.

Deposition was carried out in an oxygen atmosphere with KrF radiation (248 nm wavelength) from a Lambda Physik LPX excimer laser focused onto a rotating target of the starting material [17]. The laser-ablation target was a pellet prepared from Fisher 99.95 $TiO_2$ powder, pressed and then sintered for 6 h at 1000°C. The deposition conditions for our films are summarized in Table 1. Three types of substrate were used: (111)-oriented silicon, fused quartz, and sapphire. The thickness of the PLD films (200 nm) was estimated by ellipsometry and by interference fringes observed in reflectivity. The structure of the films was investigated by X-ray diffraction (XRD) and Raman scattering experiments. The XRD measurements were carried out with a Scintag XDS-2000 diffractometer using Cu radiation at 1.54 Å. The Raman measurements were carried out with a Dilor XY Raman microprobe using the argon 514.5 nm line. Rutile and anatase pellets were prepared and used as X-ray and Raman standards. A powder derived from natural crystals provided the reference standard for brookite.

Films were deposited on silicon substrates at 750°C, using deposition conditions (Table 1) different from those typically used for PLD deposition of oxide films [17]. The films were found to be highly crystalline and to contain brookite as a major component. Fig. 1 displays X-ray diffraction results (obtained in the usual Bragg–Brentano $\theta/2\theta$ config-

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Table 1
PLD deposition conditions used to obtain $TiO_2$ brookite rich films

| | |
|---|---|
| Substrate temperature (°C) | 750 |
| Beam energy (mJ) | 900 |
| Pulse rate (Hz) | 30 |
| Oxygen pressure (mTorr) | 200 |
| Target–substrate distance (cm) | 3 |
| Deposition rate (nm/min) | 10 |
| Substrates | Si (111)<br>Fused quartz<br>Sapphire |

uration) on one of these films, along with results on the three crystalline-powder references. The main brookite lines (labeled B in Fig. 1) at 25.3° (210), 25.7° (111), 30.8° (211), and 36.2° (102) are clearly observed. Brookite lines from higher diffraction planes are also seen but are less unambiguously distinguished from the anatase and the rutile lines also present in the diffraction pattern.

Our Raman results for the same film are shown in the top panel of Fig. 2. Again, comparison is made to the three crystalline samples. The peaks present in our brookite-powder spectrum are in agreement with those observed in earlier Raman work on brookite [18,19]. Brookite Raman lines at 128, 246, 320, and 366 $cm^{-1}$ are clearly seen in our thin-film spectrum. As in the XRD spectrum of Fig. 1, anatase lines are also evident in the film's Raman spectrum of Fig. 2. However, rutile lines are not so evident in Fig. 2. As discussed in the literature [20] and as demonstrated in the bottom panel of Fig. 2, the Raman bands of rutile are unusually broad, making them difficult to discern in a crowded mixed-phase spectrum in which rutile is a minor component.

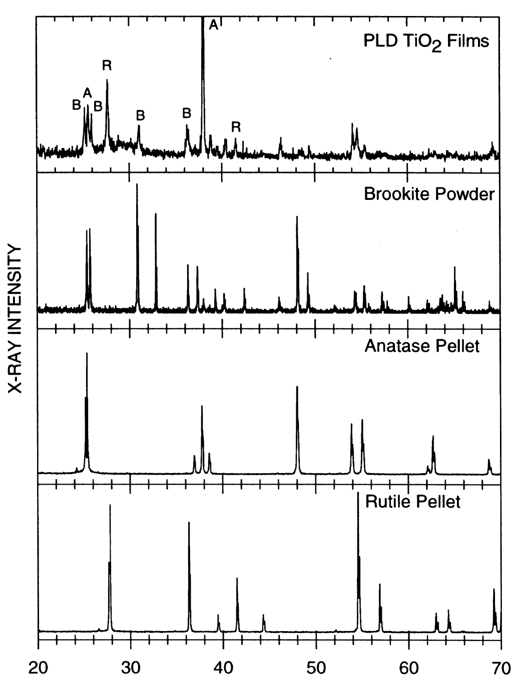


Fig. 1. X-ray diffraction results for a pulsed laser deposited $TiO_2$ thin film and for reference standards of the three crystal phases of titania. In the PLD-film spectrum, anatase, brookite, and rutile peaks are labeled A, B, and R, respectively.

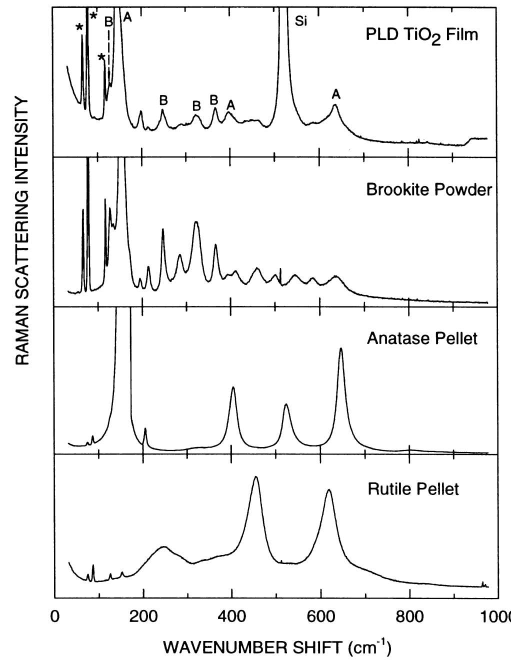


Fig. 2. Raman scattering results for the same four samples as in Fig. 1, obtained using the argon laser green line. These are Stokes spectra; wave-number shift is measured downward relative to the laser line. The three starred peaks are laser plasma lines. For the PLD thin-film spectrum, the feature labeled Si is the zone-center optical phonon line of the silicon substrate. The features labeled B and A arise from the brookite and anatase components of the film.

The predominantly brookite and anatase thin-film structure was reproduced on other silicon (111) substrates as well as on substrates of sapphire and fused quartz [21]. Also, angle-dependent XRD measurements at near-grazing incidence revealed no substantial depth dependence of the brookite/anatase/rutile mix. Peak-intensity ratios and phase mix simulations of the XRD spectra yielded the following crude estimate of the phase-mix structure for the PLD film of Figs. 1 and 2: 45 ± 15% brookite, 35 ± 15% anatase, 20 ± 10% rutile.

To summarize, we have prepared thin films of $TiO_2$ by pulsed laser deposition. X-ray diffraction and Raman scattering results show that brookite is the main phase present in the films, along with anatase and a small amount of rutile. The phase mix is not sensitive to the substrate material or the depth within the film.

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