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Phase sensitivity of Raman spectroscopy analysis of CVD titania thin films

Song Wei Lu · Caroline Harris · Scott Walck · Mehran Arbab

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Abstract Photocatalytic titania thin films deposited on float glass by chemical vapor deposition were analyzed by transmission electron microscopy, atomic force microscopy, Raman spectroscopy, and X-ray diffraction. Raman spectroscopy results indicate its phase sensitivity in the presence of trace amount of anatase. This suggests a preferable method of using Raman spectroscopy to characterize mixed phases of titania thin films, especially when titania coatings are deposited on other crystalline oxide materials, for example, tin oxide.

Introduction

Since the discovery of UV-induced photocatalytic properties of titanium dioxide by Fujishima and Honda in 1972 [1], research on photocatalysis and hydrophilicity of titania has attracted extensive attention worldwide. Titania thin films on float glass for "self-cleaning" applications and titania nanocrystalline powders have been commercially available for several years [2, 3]. The UV-induced hydrophilicity of titania films on glass results in a "sheeting" effect of water when sprayed on the coating surface to rinse dirt already on the coating surface and to greatly reduce the "spotty" dirt from water. In the meantime, organic dirt will be degraded to carbon dioxide and water by the titania coating via UV-induced photocatalysis. The photocatalytic activity of titania thin films may be affected by film thickness, microstructure, substrate, the deposition conditions, etc. The crystal phase, i.e., anatase, rutile, brookite, or a mixture of these phases, plays an important role in photocatalytic activity. Traditionally, a common method of phase determination of titania thin films is X-ray diffraction (XRD). Recently, Raman spectroscopy has been used to distinguish the anatase structure from the rutile structure [4]. This is because anatase and rutile have their own characteristic Raman active bands, which do not overlap each other.

There have been several studies of titania thin films using Raman spectroscopy. Karunagaran et al. [5] indicated that the increase in Raman band intensity and the decrease in full-width at half maximum (FWHM) could be attributed to the increase in the grain size of the annealed films on Si wafers. Wang et al. [6] studied the temperature-dependence of Raman scattering of nanocrystalline anatase, showing the shift of the E_g band from 143 cm^{-1} at room temperature to larger wavenumbers with increasing temperature.

In this article, we describe the phase sensitivity of Raman spectroscopy in analyzing commercially available chemical vapor deposition (CVD) titania thin films on clear float glass, and compare Raman results with the XRD determination of titania crystal phases. These CVD titania thin films were also characterized by transmission electron microscopy (TEM), and atomic force microscopy (AFM).

Experimental

Two commercially available titania-coated samples A and B were evaluated as-received from two difference sources. Both samples were prepared by a CVD process on float glass. As we will show below, the titania layer of sample A was deposited directly on the float glass surface, while in

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S. W. Lu (✉) · C. Harris · S. Walck · M. Arbab
Glass Technology Center, PPG Industries, Inc., 400 Guys Run Road, Cheswick, PA 15024, USA
e-mail: slu@ppg.com

Sample B, an intermediate thin film layer was deposited below titania. Sample C was prepared by depositing a titania coating under similar conditions as for sample A, but on a tin oxide layer already coated on the float glass substrate. The samples were cleaned by a mixture of 50 vol.% iso-propoxide and 50 vol.% deionized water before all characterizations.

Cross sections were analyzed with TEM using a JEOL 2000FX system with an accelerated voltage of 200 kV. Gold coating was first deposited on the sample surface in order to increase the TEM image contrast. The samples were thinned down by Ar ion milling with a Bal-tec system and then placed on a copper grid. AFM 3-D images were obtained in an MD-3000 Digital Instruments Nanoscope instrument from a 1 in. × 1 in. area. XRD characterizations were carried out in a PANalytical X'Pert MPD Difftractometer with a scan speed of 0.02°/s between 20 and 60° on a 1 in. × 1 in. sample. Raman spectra were collected using a Renishaw 2000 confocal Raman microprobe. The samples were excited by an Argon ion (514 nm) laser, whose source was focused onto the surface using a 50× (0.85 N.A.) objective to produce an approximate beam diameter of 2 μm at the sample. The power at the sample did not exceed 6 mW. The same objective was employed to collect the scattered radiation. Spectra were collected at 4 cm^{-1} resolution and represent the average of 15 individual scans. The integration time for each spectral element was 30 s.

Results and discussion

Figure 1 shows cross-sectional TEM images of samples A and B. Sample A has an approximately 23-nm thick titania coating on the glass substrate. The coating appears dense and smooth. Sample B has an undercoating layer of silicon oxy-carbide of about 50 nm, and its titania coating is about 30 nm with a rough surface. The roughness of the two coatings was independently measured by AFM analysis as shown in Fig. 2, with sample A having a RMS roughness of 0.37 nm, and sample B having a RMS roughness of 1.50 nm. In addition, AFM images suggest that the crystallite size for sample B is larger than that for sample A.

XRD patterns of both samples A and B are shown in Fig. 3, along with a sample C of 48 nm CVD TiO_2 coating on a tin oxide coating on float glass. Both samples A and B display only the anatase phase of titania. There is an extra peak of anatase from sample B, possibly due to its slightly higher thickness or a better crystallization. Sample C is a CVD titania coating on tin oxide-coated float glass. Besides the cassiterite peaks from this sample, which are due to the tin oxide layer, there are also peaks from rutile titania,

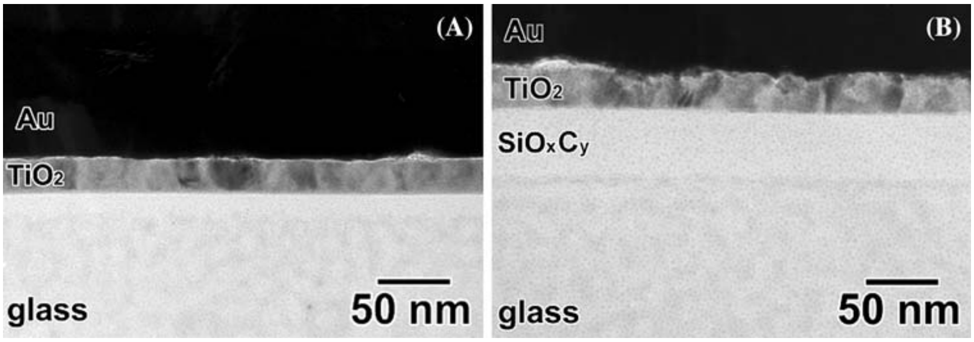

Fig. 1 Cross-sectional TEM images of samples A and B

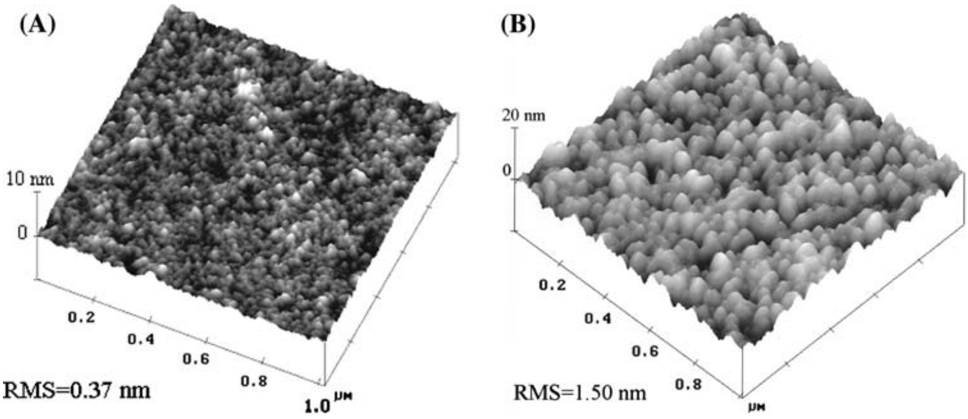

Fig. 2 AFM images of samples A and B (*Note*: the *z*-axis is 10 nm per unit for sample A, and 20 nm per unit for sample B)

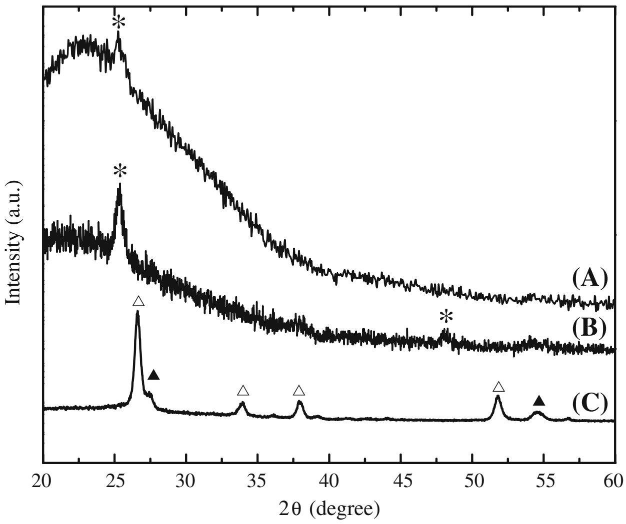

Fig. 3 XRD patterns of samples A and B, along with sample C, which is a CVD TiO_2 coating on SnO_2-coated float glass. Crystalline phase indicators: * anatase TiO_2, ▲ rutile TiO_2, and △ cassiterite SnO_2

indicating the existence of the rutile phase in the CVD titania coatings on tin oxide-coated float glass. This is mainly due to the heteroepitaxy caused by the lattice similarity between rutile titania and cassiterite tin oxide [7]. No anatase phase was measurable on this sample.

Raman spectra of samples A and B are compared to those of uncoated glass, and pure rutile titania and anatase titania (Fig. 4). Raman bands from standard anatase titania (curve 5 in Fig. 4) are located at 143 cm^{-1} (E_g), 197 cm^{-1} (E_g), 396 cm^{-1} (B_{1g}), 515 cm^{-1} (A_{1g} or B_{1g}), and 638 cm^{-1} (E_g) [8, 9]. Raman bands from standard rutile titania (curve 4 in Fig. 4) are located at 439 cm^{-1} (E_g), 611 cm^{-1} (A_{1g}), and 805 cm^{-1} (a weak shoulder, B_{1g}) [8, 9]. Sample A has Raman bands located at 147, 399, 523, and 638 cm^{-1}, along with other bands from glass itself. Similarly, sample B has Raman bands located at 146, 398, 522, and 642 cm^{-1}, along with other bands from uncoated float glass. The Raman bands from samples A and B can be attributed to Raman active modes E_g (147 cm^{-1}), B_{1g} (398 cm^{-1}), A_{1g} and B_{1g} (515 am^{-1}), and E_g (640 cm^{-1}) of anatase titania [8]. No Raman band from the rutile structure was observed for sample A (curve 1). The Raman bands for sample B are stronger than those from sample A, particularly the bands at 398 and 640 cm^{-1}. This is mainly caused by the grain size of anatase titania of the sample B, which is larger than that of the sample A, and/or by the slightly higher thickness or larger crystallite size of the titania coating in sample B than that in the sample A.

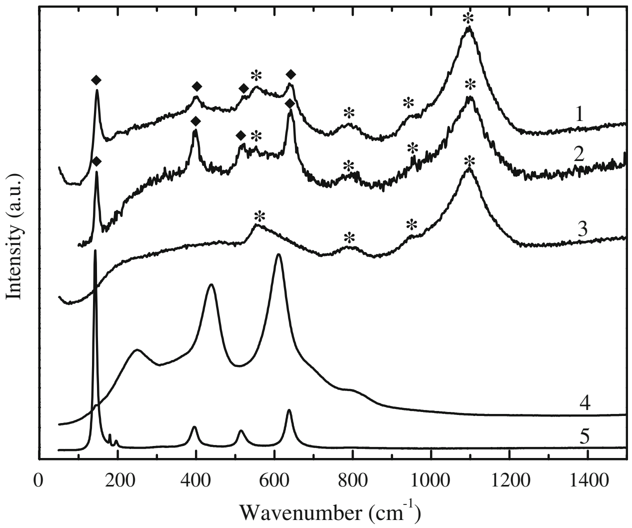

Fig. 4 Raman spectra of samples A and B, along with those from uncoated float glass, pure rutile titania, and pure anatase titania. *1* sample A, *2* sample B, *3* uncoated clear float glass, *4* rutile titania, and *5* anatase titania. * bands from uncoated clear float glass, ◆ bands from anatase titania

The Raman bands from glass itself could be assigned as an asymmetric stretching mode of Si–O–Si group (1097 cm^{-1}), the bending vibration of the Si–O–Si group (788 cm^{-1}), the rocking vibration of the Si–O–Si group, and the non-bridging silicon–oxygen bond (557 cm^{-1}) [10]. The Raman E_g band located at 196 cm^{-1} observed in the spectrum of standard anatase was absent from thin film spectra of samples A and B, probably because it is too small to be detected [4, 5, 8]. The origin of the Raman band from the standard anatase located at 180 cm^{-1} is unclear.

In Fig. 5, the Raman spectra are enlarged in the region between 110 and 180 cm^{-1}. The spectra show a shift in the Raman band positions from 143 cm^{-1} for the standard anatase titania to 146 cm^{-1} for sample B, and 147 cm^{-1} for the sample A. The figure also indicates an increase in the band width of the thin film samples. The FWHM of these Raman bands widens from 9.0 cm^{-1} for the standard

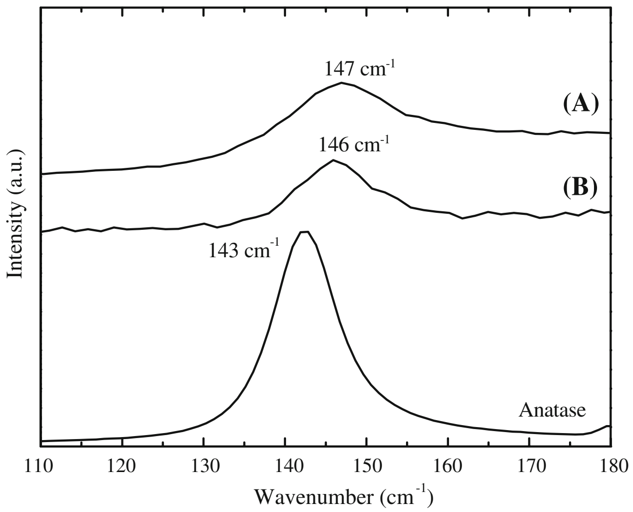

Fig. 5 The enlarged Raman spectra between 110 and 180 cm^{-1} of samples A and B as compared with standard anatase titania

anatase titania to 9.8 cm^{-1} for the sample B and 14.3 cm^{-1} for the sample A. The widening of band width may be attributed to the very low thickness of the titania coatings, i.e., about 30 nm for sample B and about 23 nm for sample A, and the larger crystallite size of sample B compared with sample A, as indicated from the AFM images (Fig. 2). Bassi et al. [11] reported a shift of the Raman band position and an increase of the FWHM as a function of titania nanocrystal sizes. For stoichiometric titania nanocrystals produced by flame pyrolysis, the E_g band position shifted from 144 to 146 cm^{-1}, and its band FWHM increased from 12 to 23.2 cm^{-1}, when reducing the nanocrystal size from 34 to 8 nm [11]. By attributing the broadening and shift of the Raman peak mainly to the particle size, Pottier et al. [12] pointed out that Raman spectroscopy is a very useful technique for characterizing particle size and crystallinity of stoichiometric anatase particles at nanoscale. Choi et al. [13] attributed the Raman band shift and broadening to the effects of decreasing particle size on the force constants and vibrational amplitudes of the nearest neighbor bonds. This study provides evidence for a similar Raman sensitivity in the case of titania thin films, which, at least in the dimension perpendicular to the substrate, are of similar scale to the previous studies on nanoparticles of titania.

The Raman spectrum of a CVD titania coating on tin oxide-coated clear float glass (sample C) is presented in Fig. 6, along with spectra of uncoated clear float glass, standard rutile titania, and anatase titania. The spectrum from the CVD titania on tin oxide-coated glass shows the co-existence of both anatase and rutile phases with a weak Raman anatase band located at 147 cm^{-1}, and two rutile bands located at 445 cm^{-1} (assigned to E_g band of rutile titania) and 609 cm^{-1} (assigned to A_{1g} band of rutile titania). By comparison, the XRD patterns in Fig. 3 show no indication of anatase in sample C. A possible scenario for the presence of both anatase and rutile phases may be that when titania was first deposited on the crystalline tin oxide coating, rutile is initially epitaxially formed because of the similarity of the crystal structure between cassiterite tin oxide and rutile titania [7]. This may then be followed by the further growth of anatase phase, which is the usual phase when depositing titania under similar conditions (i.e. the sample A). It is clear that Raman spectroscopy is very sensitive to trace amounts of anatase phase in the titania coatings, where as the XRD method used in this study was unable to detect any anatase.

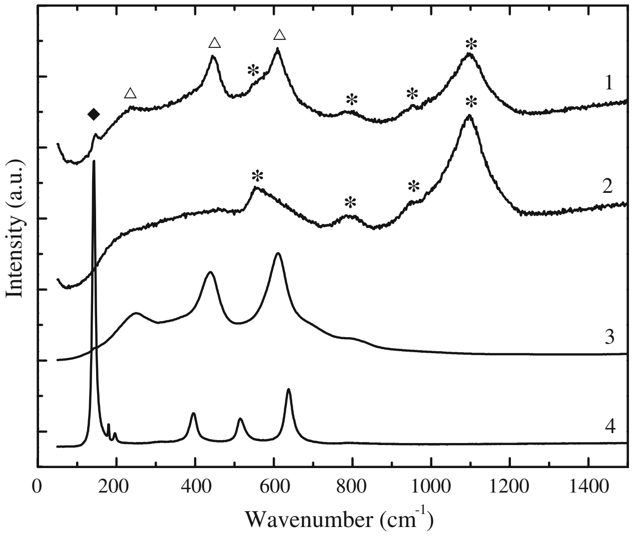

Fig. 6 Raman spectra of *1* CVD titania coatings on tin oxide-coated clear float glass (sample C), compared with *2* uncoated clear float glass, *3* standard rutile titania, and *4* standard anatase titania

Conclusions

We have demonstrated that Raman spectroscopy is a very useful tool to characterize various crystalline phases of titania thin films on clear float glass. The phase sensitivity of Raman spectroscopy was superior for analyzing phases of titania crystals in thin films to conventional XRD method. We also reported the evidence for the sensitivity of Raman peak position and FWHM to the film structure. Further study is necessary to understand and quantitatively interpret the Raman data on thin film titania.

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