

OpenAIR@RGU

The Open Access Institutional Repository at Robert Gordon University

<http://openair.rgu.ac.uk>

This is an author produced version of a paper published in

Sensors and their Applications X: Proceedings of the 10th Conference on
Sensors and their Applications, held in Cardiff, Wales, 5-8 September
1999. (ISBN 9780750306621)

This version may not include final proof corrections and does not include
published layout or pagination.

Citation Details

Citation for the version of the work held in 'OpenAIR@RGU':

LEE, S.-K., RICE, J. H., AL-OBAIDI, A. H. R., ROBERTSON, P. K. J.
and MCSTAY, D., 1999. Raman spectroscopy of laser irradiated
titanium dioxide. Available from *OpenAIR@RGU*. [online].
Available from: <http://openair.rgu.ac.uk>

Citation for the publisher's version:

LEE, S.-K., RICE, J. H., AL-OBAIDI, A. H. R., ROBERTSON, P. K. J.
and MCSTAY, D., 1999. Raman spectroscopy of laser irradiated
titanium dioxide. In : N. M. WHITE and A. T. AUGOUSTI, eds.
Sensors and their Applications X: Proceedings of the 10th
Conference on Sensors and their Applications, held in Cardiff,
Wales, 5-8 September 1999. New York: Taylor and Francis. Pp.
293-298.

Copyright

Items in 'OpenAIR@RGU', Robert Gordon University Open Access Institutional Repository,
are protected by copyright and intellectual property law. If you believe that any material
held in 'OpenAIR@RGU' infringes copyright, please contact openair-help@rgu.ac.uk with
details. The item will be removed from the repository while the claim is investigated.

Copyright (1999) From (Sensors and their Applications X: Proceedings of the 10th Conference on Sensors and their Applications, held in Cardiff, Wales, 5-8 September 1999.) by (N. M. WHITE and A. T. AUGOUSTI, eds.). Reproduced by permission of Taylor and Francis Group, LLC, a division of Informa plc.

Raman spectroscopy of laser irradiated titanium dioxide

Soo-Keun Lee, James H Rice, Ala H R Al-Obaidi, Peter K J Robertson and Daniel McStay

Optoelectronic Research Centre, School of Applied Science, The Robert Gordon University, Schoolhill, Aberdeen AB251FR.

Abstract. Raman spectroscopy is applied to investigate the effect of exposure to high power laser radiation on the crystalline phases of TiO_2 . Measurement of the changes in the Raman spectra of TiO_2 with exposure to laser radiation was reported. This has proved to be a useful sensor in monitoring both the structure and the kinetics process of change in crystalline phases from anatase to rutile during exposure to laser irradiation.

1. Introduction

Titanium dioxide (TiO_2) has been extensively studied as a photocatalyst for the degradation of organic and biological complexes [1,2]. The photocatalytic activity of TiO_2 is dependant upon a number of factors such as surface area, annealing temperature and crystalline structure [1,2]. TiO_2 has three crystalline phases but commonly only two are used in photocatalytic studies - anatase and rutile [1]. The most active form of TiO_2 is reported to be Degussa P25 which has a precise mixture of anatase to rutile of ratio of 80:20 [3]. Transforming one crystalline phase of anatase to rutile to another can be achieved by the application of either high temperature or via high laser power [1]. Raman spectroscopy has been performed upon the effect of temperature on TiO_2 crystalline phases [4-6] but as far as the author is aware no Raman spectroscopy studies on the effect of intense laser irradiation upon the crystalline phases of TiO_2 has been performed which has important ramifications for its application in photocatalysis where conditions of intense irradiation may be present.

2. Experimental

2.1. Laser treatment of TiO_2

The catalyst under investigation was P25 TiO_2 which has a 80 : 20 anatase to rutile mix supplied from Degussa. The laser source for irradiation of the TiO_2 was a Continuum Surlite tripled Nd:YAG laser at 355 nm. This produced 4.5 ns pulses of 10 MW peak pulse power. Irradiation of the samples was carried out by placing 20 mg of

TiO₂ directly in the laser beam for varying times. The TiO₂ powder was shaken every two minutes during laser radiation.

2.2. Raman system.

Raman spectroscopy measurements were recorded using an Argon ion laser operating at 514 nm. The laser power was 500 mW at the sample. The laser line was filtered to remove any traces of plasma lines using a 3 nm interference filter centred at 514 nm. A silver spot mirror with 3 mm diameter was used to direct the laser beam to the sample. The laser spot size at the sample is about 25 μm in diameter which is imaged at the slit of the spectrograph (Oriel 260i spectrograph) using a back scattering geometry as shown in Figure 1. A slit width of 20 μm was used. The Raman signal was filtered before passing through the spectrograph using a notch filter. The Raman signal was detected using a water cooled front illuminated CCD detector (Oriel model DU401) cooled to -80°C and analysed using a PC as illustrated in Figure 1.

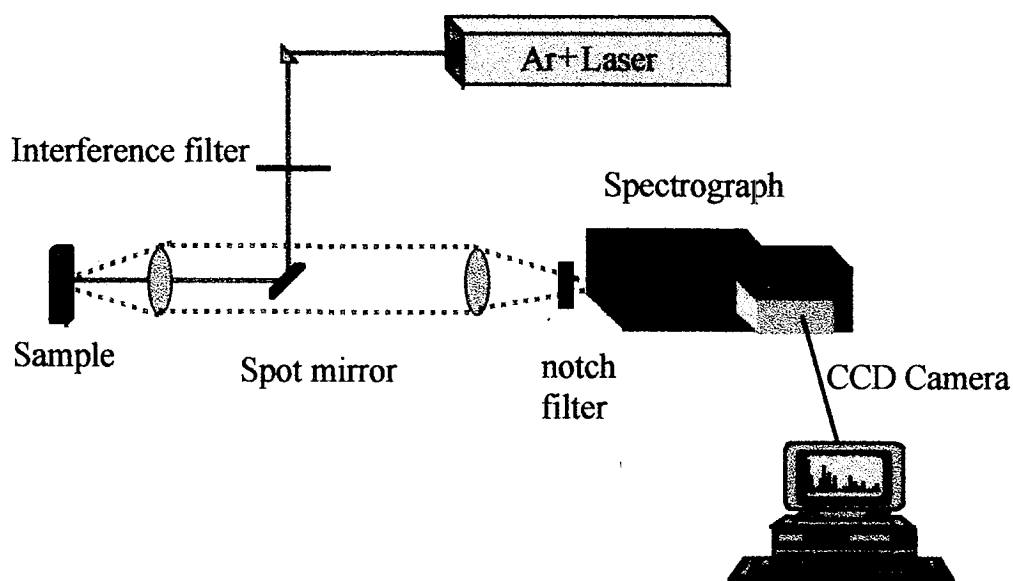


Figure 1. Schematic diagram of the Raman system.

3. Results

The Raman spectrum of TiO₂ before and after laser irradiation treatment for 10 min is shown in Figure 2. Figure 2a shows the Raman spectra of the untreated TiO₂. Several Raman bands at 166 cm⁻¹, 404 cm⁻¹, 521 cm⁻¹ and 635 cm⁻¹ are observed. These Raman bands are assigned to the anatase form of the TiO₂ [4-7]. The Raman spectra of the TiO₂ sample for irradiated for 10 minutes with the laser line at 355 nm produced a distinctive Raman spectrum as shown in Figure 2. It can be seen that the Raman bands at 166, 404, 635 cm⁻¹ were shifted to 174, 430, and 616 cm⁻¹. The Raman band at 521 cm⁻¹ was disappeared during the irradiation process and a new broad band at 1090 cm⁻¹ appeared. It has been reported that the rutile form of the

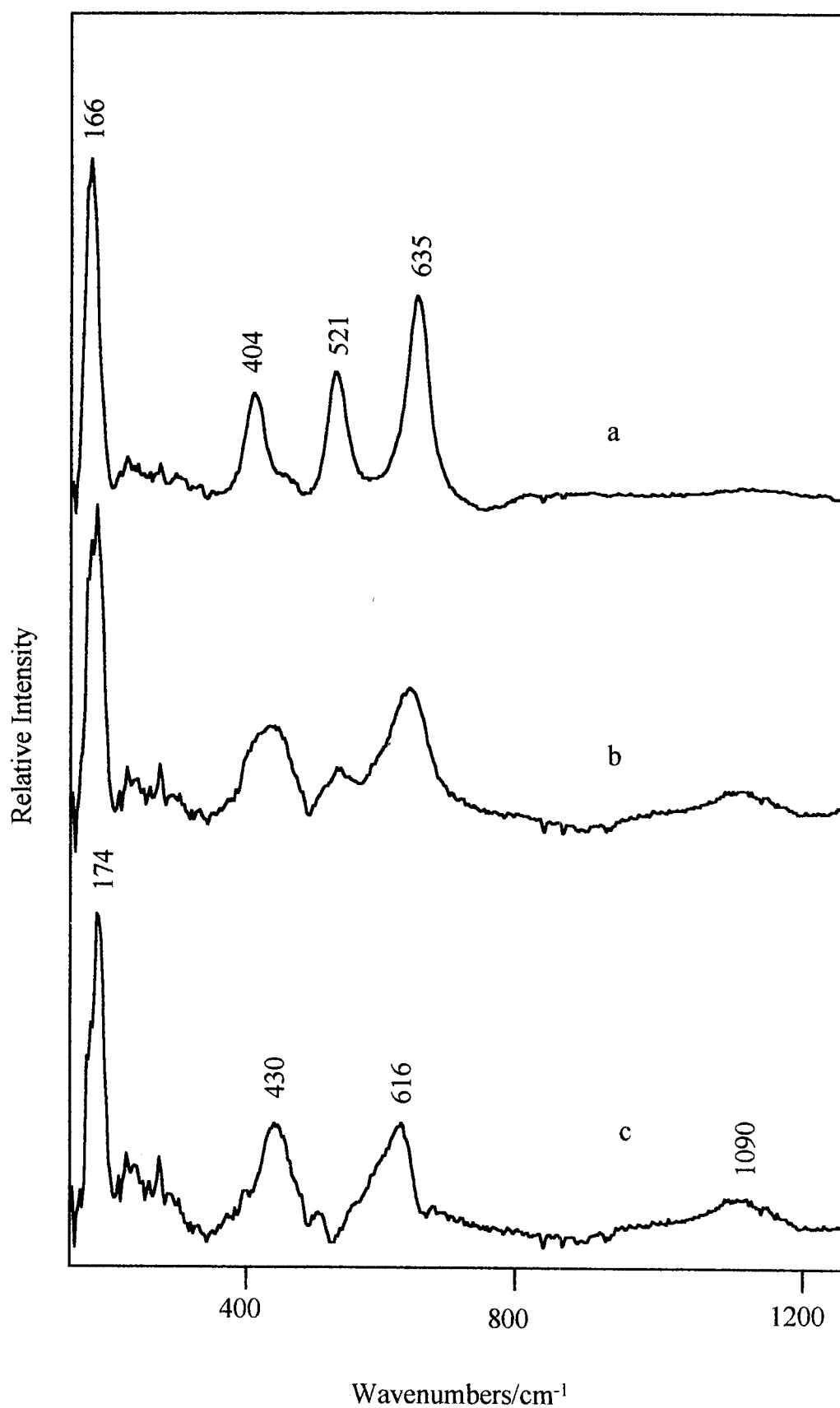


Figure 2. Raman spectra of TiO₂. (a) initial sample. (b) irradiation for 10 min (c) a-b.

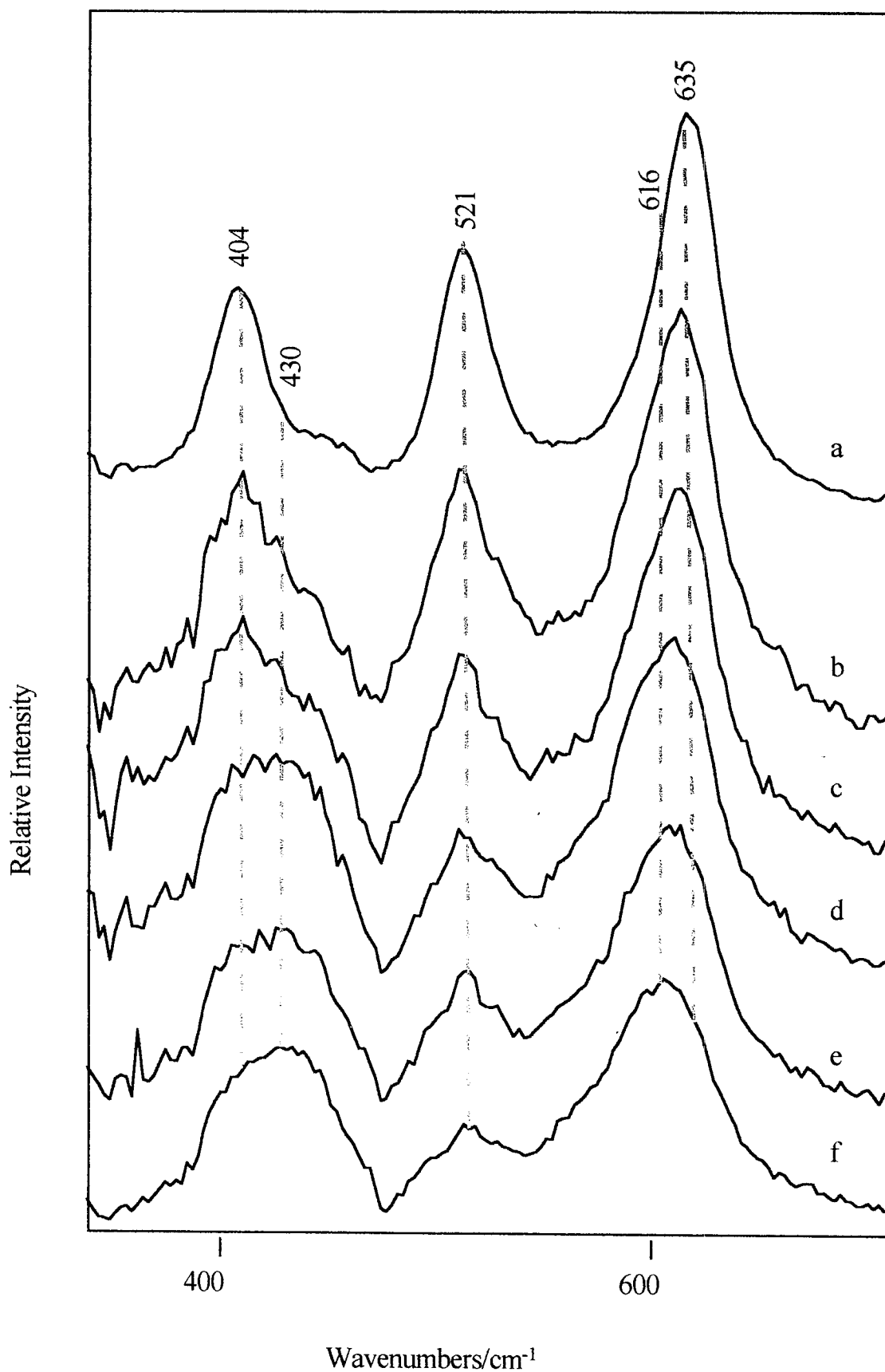


Figure 3. Raman spectra of TiO_2 , (a) initial sample, (b) irradiation for 2 min. (c) irradiation for 4 min., (d) irradiation for 6 min., (e) irradiation for 8 min. and (f) irradiation for 10 min.

TiO₂ exhibits Raman bands at 440 cm⁻¹ and 610 cm⁻¹. Therefore, the spectrum in figure 2b could be assigned to the formation of the rutile form of TiO₂. These results thus indicate that the the anatase form of the TiO₂ disappeared during the laser irradiation and converted to rutile form.

For studying the kinetics of the conversion of the anatase to rutile, the Raman spectra were recorded at several time integrals (see figure 3). Again an increase in intensity of the bands associated with the rutile form and a decrease in the intensity of the anatase form was observed.

The data shown in Figure 3 was further analysed by plotting the rise and fall of the bands at 430 and 521 cm⁻¹ respectively, which are associated with the rutile and anatase forms, (see figure 4). This clearly shows the kinetics of the conversion of the anatase to rutile as a function of time.

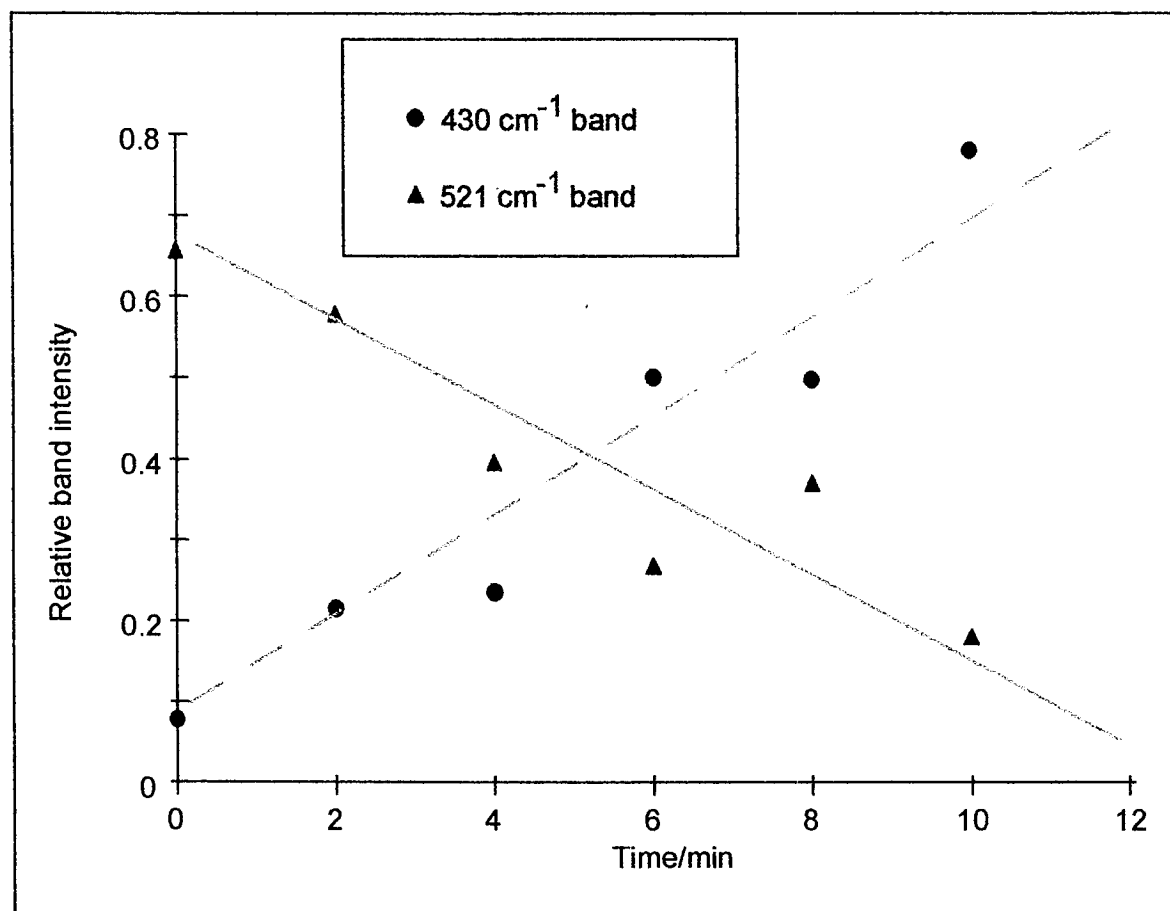


Figure 4. A plot of relative intensity of the bands at 521 cm⁻¹ and 430 cm⁻¹ against laser exposure time.

X-ray crystal data for anatase and rutile are shown table 1. [8]. This shows that a change in phase from anatase to rutile brings about a reduction in the Ti-Ti bond distance and an increase in bond length for the Ti-O bond. This data could therefore assist in assigning the Raman spectra of the TiO₂.

The data reported in this paper has shown the effect of exposing TiO₂ over time to high light intensities. The change has been assigned to a change in crystalline phase from anatase to rutile.

Table 1. Bond distance for each phase for Ti to Ti bonds and Ti to O bonds.

Phase	Bond type and length / Å			
	Ti-Ti	Ti-Ti	Ti-O	Ti-O
Anatase	3.79	3.04	1.949	1.980
Rutile	3.57	2.96	1.934	1.980

6. References.

- [1] Lee S-K, Robertson P K J, Mills A and McStay D 1999 *J. Photochem. Photobio A: Chem.* **122** 69
- [2] Mills A and Morris S 1993 *J. Photochem. Photobio A: Chem* **71** 75
- [3] Augustynski A 1993 *J. Electrochemi. Acta* **38** 43
- [4] Zang Y-H, Chan C K, Porter J F and Guo W 1998 *J. Mater. Res* **13** 2602
- [5] Gotic M, Ivanda M, Popovic S, Music S, Sekulic A, Turkovic A and Furic K 1997 *J. Raman Spec* **28** 555
- [6] Exarhos G *J. Vac. Sci* 1986 **A4** 2962
- [7] Tompsett G A, Bowmaker G A, Cooney R P, Metson J B, Rodgers K A and Seakins J M 1997 *J. Raman Spec* **26** 57
- [8] Linsebigler A L, Lu G and Yates J T 1995 *Chem. Rev* **95** 735.