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# The photochemistry of thin films of titanium diacetylacetonate diisopropoxide on silicon surfaces

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**Abstract**

The photochemistry of films of Ti(acac)$_2$(*i*-prop)$_2$ (*i*-prop = CHO(CH$_3$)$_2$; acac = CH$_3$COCHCOCH$_3$) is presented. Films of Ti(acac)$_2$(*i*-prop)$_2$ can be cast on silicon surfaces and upon irradiation in air are converted to titanium dioxide films. The organic photoproducts, which are ejected from the film, were identified by mass spectroscopy to be 2-propanone, acetylacetone and 3-pentane-2-one. The remaining product, which constituted the film, was titanium oxide which upon air oxidation is converted to amorphous titanium dioxide. Heat treatment of the titanium dioxide film resulted in the crystallization of anatase at temperatures below 700 °C and rutile at temperatures above 1100 °C. Heat treatment at intermediate temperatures resulted in the formation of mixtures of anatase and rutile. © 2002 Published by Elsevier Science B.V.

*Keywords:* Thin films; Photodeposition; Amorphous materials

## 1. Introduction

In this contribution, we will provide evidence concerning the photoreaction of films of the title complex to produce titanium dioxide films [1]. Our interest in the photochemical reaction of this complex is spurred by the demonstration that it serves a useful precursor to a variety of complex metal oxide films prepared by photochemical metal organic deposition (PMOD) [1–4]. In this process, a metal complex is deposited as a thin amorphous film on a surface and photolysis results in the loss of ligands from the surface and the production of the metal [5], or in the presence of a oxygen source, the metal oxide [5–7]. By learning the details of the reaction mechanism, we can use this information to design new precursors.

In this contribution, we will establish the photoproducts of the reaction of the title complex, Ti(acac)$_2$(*i*-prop)$_2$ (*i*-prop = CHO(CH$_3$)$_2$; acac = CH$_3$COCHCOCH$_3$). Previous studies [1] established that the product retained in the film was TiO$_2$, but the fate of the organic ligands was not determined.

In many previous studies, we had identified the organic products of PMOD depositions where the organic ligands were carboxylates [5–7]. There is less known about the photochemistry of metal β-diketonates in thin films [8–13]. The precursor studied here has similarities with other complexes reported to be suitable precursors for PMOD. For example, we have reported the photochemistry [10,11] and mechanism [12] of uranyl 1,3-diketonates for the preparation of uranium oxide by PMOD. Significantly, we found that the involvement of a coordinated water molecule was necessary to provide for the observed mechanism. We have also reported the use of aluminum 1,3-diketonate alkoxide complexes to prepare aluminum oxide films [13]. The mechanism of these reactions is still under study in our laboratory.

Also of interest for practical applications is the characterization of the behavior of the films upon annealing. We complete the present study by determining the crystalline products which can be prepared by combining the PMOD process with heat treatments of the resultant films.

## 2. Results

### 2.1. Photolysis of Ti(acac)$_2$(i-prop)$_2$ films

A toluene isopropanol solution of Ti(acac)$_2$(*i*-prop)$_2$ was used as a precursor solution. This solution was used to spin coat silicon and provided an amorphous film of Ti(acac)$_2$(*i*-prop)$_2$ on the silicon chip. The films appeared to be uniform by optical inspection.

The FTIR spectrum of a film of Ti(acac)$_2$(*i*-prop)$_2$ was obtained by measuring the transmission through the sample

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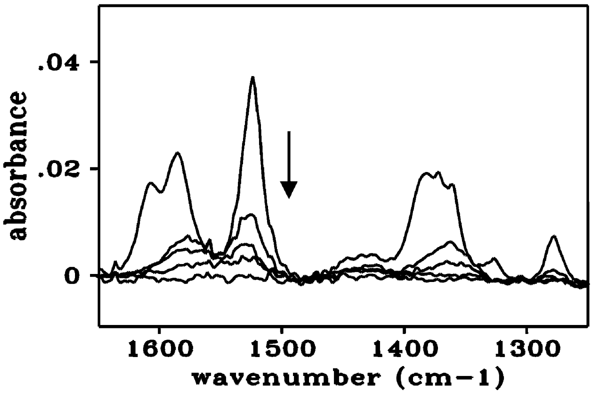


Fig. 1. FTIR spectra of a thin film of $Ti(acac)_2(i\text{-prop})_2$ following photolysis for 0, 5, 10, 15 and 25 min.

and is presented in Fig. 1. Blair and Hill [1] has produced data similar to those in Fig. 1. Assignments can be made based on various metal acetylacetonate and metal alkoxide complexes [14–16] and are in agreement with those of Blair and Hill [1].

The similarity of the spectra observed here and in solution [15], where the structure is known to have a *cis* geometry, is consistent with the compound having a *cis* orientation of the alkoxide groups. This structure is shown in Fig. 2 and assumed throughout. This assignment should be treated cautiously, however, as it is known that the *cis* to *trans* isomerism in isostructural systems may cause subtle changes in the IR of the acetylacetonate ligand [17].

The film of $Ti(acac)_2(i\text{-prop})_2$ was irradiated with 254 nm light for 5 min. A second FTIR spectrum was obtained and is presented in Fig. 1. A decrease in intensity of all the FTIR absorption bands associated with $Ti(acac)_2(i\text{-prop})_2$ is observed. The experiment proceeded with alternating exposures to UV light and spectral analysis of FTIR. Fig. 1 shows the FTIR spectral changes. A decrease in intensity of all the FTIR absorption bands associated with $Ti(acac)_2(i\text{-prop})_2$ is observed. The photolysis of $Ti(acac)_2(i\text{-prop})_2$ for a total of 25 min resulted in the loss of all IR absorption bands associated with the acetylacetonate and isopropoxide ligands. No new absorption bands were observed. This indicates that there was no thermally stable intermediates detected.

The lack of observable IR bands in the region associated with C–H and C=O stretching vibrations indicates that the organic products of the reaction have left the surface. This suggests that only the metal component of the precursor remains on the surface. This result forced us to turn to a different method to investigate the organic photoproducts.

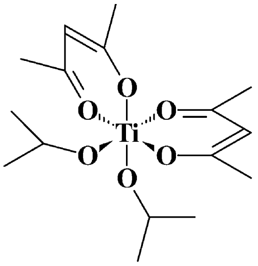


Fig. 2. Diagram showing structure of a $Ti(acac)_2(i\text{-prop})_2$ within a film.

### 2.2. Mass spectrometric analyses of volatile photoproducts formed by the photolysis of $Ti(acac)_2(i\text{-prop})_2$ film

Mass spectrometric analysis of the volatile products formed from photolysis of a $Ti(acac)_2(i\text{-prop})_2$ film on a silicon chip was conducted in order to determine the organic photoproducts. A $Ti(acac)_2(i\text{-prop})_2$ film on a silicon chip was irradiated with 254 nm light in a vacuum chamber. The gaseous contents of the chamber were then introduced into a mass spectrometer.

The spectrum of MS had peaks at $m/e$ of 100, 85, 84, 69, 58, 43 and 41. The peaks at $m/e$ of 100, 85 and 43 are associated with acetylacetone ($CH_3COCH_2COCH_3$, $m/e = 100$) and its fragments, $COCH_2COCH_3$ ($m/e = 85$) and $COCH_3$ ($m/e = 43$). The peaks at $m/e$ of 84, 69, 43 and 41 corresponded to 3-pentene-2-one ($CH_3COCH{=}CHCH_3$, $m/e = 84$) and its fragments, $COCH{=}CHCH_3$ ($m/e = 69$), $CH_3CO$ ($m/e = 43$) and $CH{=}CHCH_3$ ($m/e = 41$). The peaks at $m/e$ of 58 and 43 corresponded to 2-propanone ($CH_3COCH_3$, $m/e = 58$) and its fragment, $COCH_3$ ($m/e = 43$). Table 1 summaries the data and interpretation [18,19] of the mass spectrum of the volatile products from photolysis of the $Ti(acac)_2(i\text{-prop})_2$ film.

The identified photoproducts and the FTIR of the surface are consistent with the photochemical reaction shown as Eq. (2). The organic photoproducts are 2-propanone, acetylacetone and 3-pentane-2-one. In order to balance the reaction, two molecules of 2-propanone, formed hydrogen abstraction from the isopropoxide ligand, are formed. The hydrogen lost from the isopropoxide ligand contributes to the formation of one equivalent each of acetlyacetone and 3-pentene-2-one. The surface film must retain an oxygen atom, from one of the acetylacetonate ligands, in order to balance the reaction. This retained oxygen is presumably in the form of titanium(II) oxide, as Ti(II) oxide. In order to test this hypothesis, Auger electron spectra were collected.

$$Ti(CH_3COCHCOCH_3)_2(OCH(CH_3)_2)_2 \xrightarrow{h\nu} TiO + CH_3COCH{=}CHCH_3 + CH_3COCH_2COCH_3 + 2CH_3COCH_3 \qquad (1)$$

Table 1
Mass spectral data from the volatile products produced in the photolysis of a film of $Ti(acac)_2(i\text{-prop})_2$

| $m/e$ | Assignment |
|---|---|
| 100, 85, 43 | Acetylacetone ($MeCOCH_2COMe$) |
| 84, 69, 43, 41 | 3-Pentene-2-one ($MeCOCH{=}CHMe$) |
| 58, 43 | 2-Propanone (MeCOMe) |

Table 2
Auger electron spectroscopic data from a film resultant from photolysis of a film of $Ti(acac)_2(i\text{-prop})_2$ on silicon

| Sputter time (s) | Intensity | | Concentration (sensitivity) | | Composition |
|---|---|---|---|---|---|
| | Ti (LMM) | O (KLL) | Mn (0.45) | O (0.51) | |
| 15 | 19.5 ± 5 | 70.4 ± 5 | 23 ± 6 | 77 ± 5 | $Ti_6O_{19}$ |
| 30 | 20 ± 6 | 69 ± 6 | 25 ± 7 | 75 ± 6 | $TiO_3$ |

### 2.3. Auger electron analyses of films produced by the photolysis of a $Ti(acac)_2(i\text{-prop})_2$ film

In order to determine the elemental composition of the remaining film after $Ti(acac)_2(i\text{-prop})_2$ photolysis, Auger electron analyses were carried out. Argon ion sputtering for 15 s cleaned the surface. An Auger electron spectrum of the exposed surface was then obtained.

The Auger electron spectrum of the sample prepared above was then recorded. The spectrum has peaks at 380, 418 and 502 eV. Peaks at 380, 418 eV are associated with titanium (LMM) and the peak at 502 eV is indicative of oxygen (KLL) [20]. No other peaks were observed in the spectrum. This indicates that the only elements existing on the film are titanium and oxygen. Table 2 lists the sputter time, peak intensity, sensitivity factor and atomic concentration of titanium and oxygen. It also includes the composition of the film obtained from the experiment. The calculated compositions were based upon the intensity of the oxygen signal at 502 eV and the titanium signal at 418 eV. The calculated composition of the film from two spectra was $TiO_{3\pm1}$. The film probably consisted of titanium(IV) oxide, as Ti(IV) oxide is the most stable oxidation state of titanium [21]. The reported results of Blair and Hill [1] are within experimental error of those determined here.

The next experiment was done to investigate if there was a composition dependence upon the position within the film. The sample was subjected to a further 15 s of sputtering. This exposed a region of the film further from the initial surface. The Auger spectrum of this region was obtained. The only elements detected were titanium and silicon. The analysis of the intensity indicated that the elemental composition was within error of the previously analyzed region.

These analysis indicate that the film is not Ti(II) oxide, but rather Ti(IV) oxide. This suggests that the initially formed Ti(II) oxide film undergoes oxidation to yield Ti(IV) oxide. The film was then analyzed by X-ray diffraction.

### 2.4. X-ray diffraction from the films produced by the photolysis of $Ti(acac)_2(i\text{-prop})_2$

The sample of Ti(IV) oxide produced above was analyzed by X-ray diffraction. The only reflections observed were from the silicon substrate. No reflections indicative of crystalline titanium dioxide were detected. This indicated that the film was amorphous Ti(IV) oxide. This data indicates that the overall photoreaction is best represented as Eq. (2).

$$\begin{aligned} &Ti(CH_3COCHCOCH_3)_2(OCH(CH_3)_2)_2 + \tfrac{1}{2}O_2 \\ &\xrightarrow{h\nu} TiO_{2(\text{amorphous})} + CH_3COCH{=}CHCH_3 \\ &\quad + CH_3COCH_2COCH_3 + 2CH_3COCH_3 \end{aligned} \tag{2}$$

In order to study the crystallization of the amorphous Ti(IV) films, XRD spectra were obtained on a series of heated films. An amorphous Ti(IV) oxide film was heated at 300 °C for 2 h. Fig. 3(a) shows the XRD spectrum collected on the film after heating. The reflection at 33° was from the *n*-Si(1 0 0) substrate. No reflections attributable to crystalline titanium dioxide were observed. This indicated that the film still was amorphous after 300 °C heating.

In a similar experiment, a Ti(IV) oxide film was prepared and heated at 500 °C for 2 h. Fig. 3(b) shows the XRD spectrum collected on the film. Reflections were observed at angles, 2$\theta$, of 25, 38, 48, 54 and 55°. They corresponded to reflections from the anatase (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) planes [22]. This data indicated that the amorphous film crystallized to yield polycrystalline anatase as a result of the thermal treatment. In a similar experiment, a photoproduced amorphous titanium oxide film was heated to 700 °C. The XRD spectrum, Fig. 3(c) indicated reflections at the same angles as found following heating at 500 °C. This indicates that polycrystalline anatase was formed by heating to 700 °C.

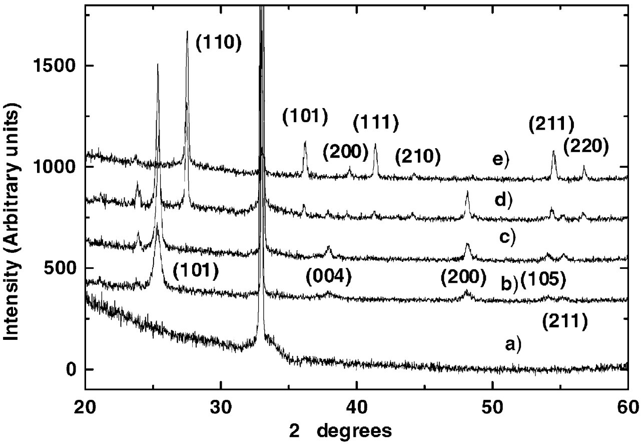


Fig. 3. X-ray powder diffraction spectra of titanium dioxide films after being heated for 2 h at (a) 300 °C, (b) 500 °C, (c) 700 °C, (d) 900 °C, and (e) 1100 °C.

A film of amorphous Ti(IV) oxide was also heated at 900 °C for 2 h. Fig. 3(d) shows the XRD spectrum collected on the film. In this figure, reflections at Bragg angles (2$\theta$) of 25, 38, 48, 54 and 55° are apparent. These corresponded to reflections from the anatase planes described in the previous sections. The X-ray diffraction spectrum also shows reflections at Bragg angles of 27, 36, 39, 41, 44, 54 and 57°. These correspond to reflections from the (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 0), (2 1 1) and (2 2 0) planes of rutile [23]. This indicated that the film was composed of a mixture of anatase and rutile.

A film prepared the same way as above was heated at 1100 °C for 2 h. Fig. 3(e) shows the XRD spectrum. This diffractogram shows reflections at angles, 2$\theta$, of 27, 36, 39, 41, 44, 54 and 57°. These, as assigned earlier, are associated with reflections from polycrystalline rutile.

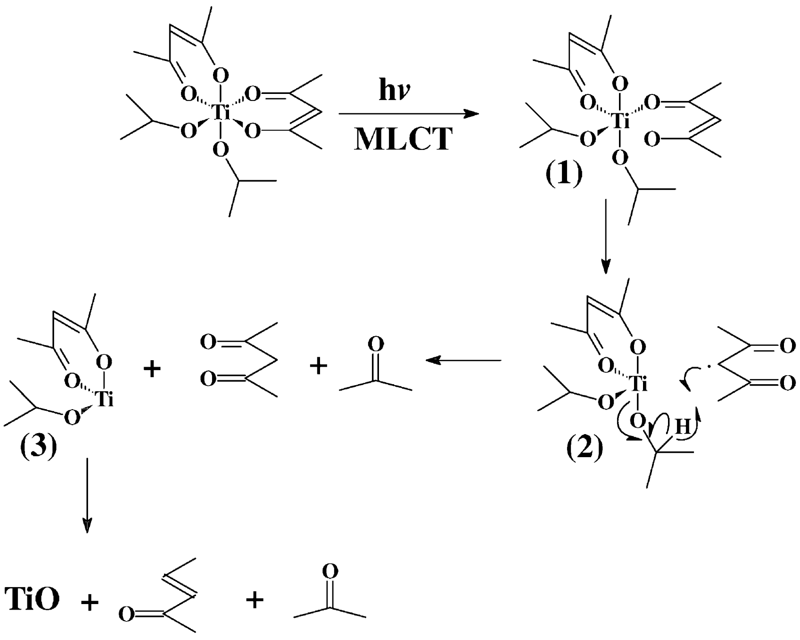
## 3. Discussion

It has been shown that the Ti(acac)$_2$($i$-prop)$_2$ precursor solution could form a uniform film through spin coating. The structure of the complex in the film was presumably the *cis*-Ti(acac)$_2$($i$-prop)$_2$ isomer. The evidence from IR is not unambiguous, however, other factors to support the assignment of a *cis* geometry. The *cis* isomer is the more stable electronically [15], while the *trans* isomer is sterically preferred. The *cis* structure has been identified crystallographically in similar titanium dialkoxide bis-β-diketonates [24,25]. In one of these cases [25], the ligand environment was more crowded that the derivative studied here yet the structure was *cis*.

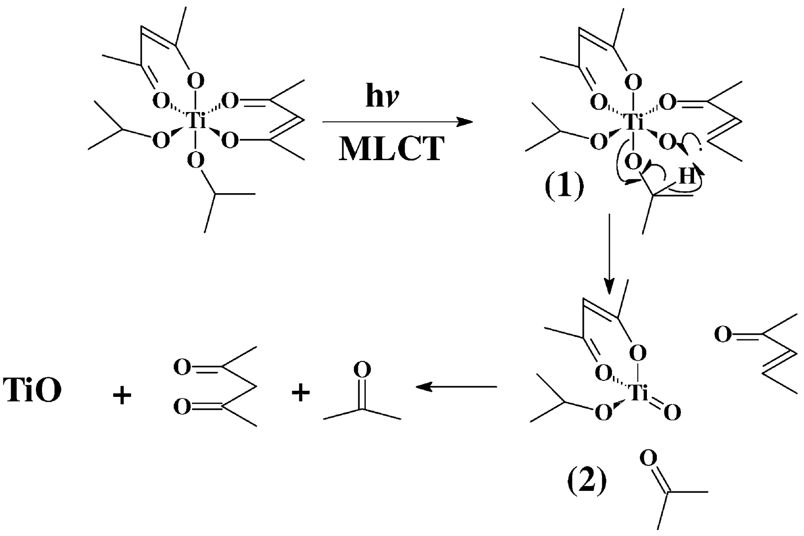
FTIR spectroscopy indicated that all the organic ligands of Ti(acac)$_2$($i$-prop)$_2$ have been ejected from the film upon irradiation with 254 nm light. The products of the reaction, acetylacetone, 3-pentene-2-one, 2-propanone and Ti(II) oxide, were not anticipated based upon the previous work [1]. In past work, the ligands were assumed to have retained the oxygen atom and produce titanium which was oxidized by atmospheric oxygen. Here, we have presented evidence suggesting that the acetylacetonate ligand can separate from the titanium by cleaving a carbon–oxygen bond. The result of this is to generate Ti(II) oxide and, following H-atom transfer from an isopropoxide ligand, 3-pentene-2-one. A mechanism for the photo-decomposition of Ti(acac)$_2$($i$-prop)$_2$ which would account for these results is shown in Scheme 1.

The reaction is initiated by the absorption of a photon which results in a ligand-to-metal charge transfer transition in the starting material, Ti(acac)$_2$($i$-prop)$_2$. The transition results in cleaving a titanium oxygen bond between the titanium and an acetylacetonate ligand. Upon cleavage the diradical species (**1**) is formed. The complex (**1**) contains both an organic centered radical and a titanium in the +3 oxidation state. As a result, we expect (**1**) to be very reactive. The unstable species (**1**) fragments to form (**2**) and the acetylacetonyl radical (**3**). The acetylacetonate radical may abstract a hydrogen from the isopropyl ligand yielding acetylacetone, 2-propanone and compound (**3**). Compound (**3**) is a Ti(II) complex and further decomposes. Compound (**3**) may cleave the remaining acetylacetonate ligand driven by the formation of titanium oxide. The organic products from this step, 3-pentene-2-one and 2-propanone, are formed as a result of a hydrogen abstraction from the isopropoxide group.

While this mechanism provides insight into the nature of the fragmentation process, there is little evidence for the



Scheme 1. Illustration of reaction mechanism for the photoreaction of Ti(acac)$_2$($i$-prop)$_2$ within a film.



Scheme 2. Illustration of alternate reaction mechanism for the photoreaction of Ti(acac)$_2$(*i*-prop)$_2$ within a film.

temporal order of the fragmentation. The choice of the order of the fragmentation, in particular, the proposal that it is the second acetylacetonate ligand which is lost by carbon oxygen bond cleavage, is somewhat arbitrary. This is proposed as it seems reasonable that it would be this latter intermediate with the greater thermodynamic driving force to form titanium oxide.

An alternate order, illustrated in Scheme 2, would involve a photochemical cleavage of the carbon oxygen bond of an acetylacetonate ligand forming the titanium oxygen double bond forming intermediate (**1**). The intermediate (**1**) undergoes an internal hydrogen atom abstraction to yield intermediate (**2**), 3-pentene-2-one and 2-propanone. The titanium in intermediate (**2**), is Ti(IV) and four coordinates. To explain the observed products, Scheme 2 shows this intermediate decomposes yielding TiO, acetylacetone and 2-propanone. It is not obvious that this intermediate (**2**) in Scheme 2, should be so unstable and so the mechanism presented in Scheme 1 appears more reasonable.

It is interesting to note the range of products which have been identified to result from the photochemical reaction of different metal acetylacetonates as films. The reaction of $UO_2(OH_2)$(acac)$_2$ led to the formation of $UO_3$, acetylacetone and 3-hydroxy-3-methylcyclobutanone [12]. Interestingly, the coordinated water contributed two hydrogen atoms to the organic products. In the case of Ti(acac)$_2$(*i*-prop)$_2$, studied herein, the two isopropoxide ligands each supplied one hydrogen atom. In spite of this similarity, the organic products were different. It will be interesting to examine the photoproducts of other metal acetylacetonate thin films to see if a trend emerges.

The photoreaction of Ti(acac)$_2$(*i*-prop)$_2$ film resulted in the formation of Ti(II) oxide in the film. The photoproduced Ti(II) oxide reacts with oxygen in air to generate the Ti(IV) oxide film. X-ray powder diffraction indicated that the Ti(IV) oxide film was amorphous. Heating the amorphous film resulted in its crystallization. Crystallization temperature has a strong influence on the structure of the films. At crystallization temperatures of 500 and 700 °C, polycrystalline anatase was formed. At intermediate temperatures between 700 and 1100 °C both anatase and rutile were found. Heating in air up to 1100 °C resulted in the observation of exclusively polycrystalline rutile.

These observations are as consistent with the phase diagram of Ti(IV) oxide [26]. The effect of annealing is to initially form the anatase structure. This phase converts to the thermodynamically more stable rutile structure upon heating [27]. These results are consistent with those of Martin et al. [28] who have studied $TiO_2$ films deposited by reactive rf magnetron sputtering. In these studies, a temperature dependence on the amount of anatase and rutile in the products was found. The temperature to transform anatase to rutile has been shown to depend on the method of preparation of the sample [29].

## 4. Conclusion

The photochemical deposition of titanium dioxide films from thin films of Ti(acac)$_2$(*i*-prop)$_2$ has been demonstrated. The photochemistry of Ti(acac)$_2$(*i*-prop)$_2$ has been studied by FTIR, mass spectroscopy and Auger electron spectroscopy. The Ti(acac)$_2$(*i*-prop)$_2$ precursor film absorbs photons upon UV irradiation undergoing a ligand-to-metal charge transfer transition. This transition finally leads to the generation of titanium oxide acetylacetone, 2-propanone and 3-pentene-2-one. The photoproduced titanium oxide film reacts with $O_2$ in air resulting in amorphous films of titanium dioxide. Anatase and rutile were successfully formed upon thermal heating of the amorphous titanium dioxide. At low temperatures, anatase was formed. At intermediate temperatures, an anatase–rutile mixture was formed while at high temperatures rutile was formed.

## 5. Experimental

The n-type Si(1 0 0) wafers obtained from Shin Etsu were cleaned by acetone before use. The silicon was cut to the approximate dimensions 10 mm × 14 mm. An in house built spin coater was used to coat films on the silicon chips. The Ti(acac)$_2$(*i*-prop)$_2$ precursor was obtained commercially from Aldrich Co., as a solution in isopropanol. The photolysis of the Ti(acac)$_2$(*i*-prop)$_2$ film was monitored by FTIR spectroscopy. The photolysis beam was from a UVP Inc., model UVG-54 short wave UV-254 nm lamp. The FTIR spectra were obtained with 4 $cm^{-1}$ resolution using a Bomem MB-120 FTIR spectrophotometer.

The mass spectra were recorded with a HP 5958 gas chromatography (GC)–MS spectrometer. An electron-impact ion source was used and the ion source temperature was 200 °C. The electron energy for ionization was 70 eV. The scanning mass range was 5–120 *m*/*z*. Auger spectra were obtained using a PHI double pass CMA at 0.85 eV resolution at the Surface Analysis Laboratory, Department of Physics, Simon Fraser University. XRD spectra were obtained using a X-ray generator system (model: PW1730 Philips Electronic Instruments Inc.) with Cu K$\alpha$ radiation, Department of Physics, Simon Fraser University.

### *5.1. Preparation and photolysis of Ti(acac)$_2$(i-prop)$_2$ films*

An FTIR spectrum of a silicon chip was obtained prior to the film deposition and used as a reference. The silicon chip was placed on the platform of the spin coater. It was secured on the platform with double-sided tape. A few drops of a solution of Ti(acac)$_2$(*i*-prop)$_2$ (0.1230 g) in toluene (1.2401 g) were dispensed from a disposable pipette onto the stationary silicon chip. The sample was then spun at 2800 rpm for approximately 1 min.

An FTIR spectrum of the film was obtained. The sample was irradiated with 254 nm light for 5 min. Another FTIR spectrum was obtained. This procedure was repeated for accumulated photolysis times of 10, 15 and 25 min at which time the FTIR bands due to the ligands in the Ti(acac)$_2$(*i*-prop)$_2$ were no longer observed (see Fig. 1).

### *5.2. Mass spectrometric analysis of volatile products produced in the photolysis of Ti(acac)$_2$(i-prop)$_2$ films*

The volatile photoproducts from a film of Ti(acac)$_2$(*i*-prop)$_2$ on a silicon chip were analyzed with a mass spectrometer. A film of Ti(acac)$_2$(*i*-prop)$_2$ on a silicon chip was placed into a vacuum chamber, evacuated and irradiated with 254 nm light for 25 min.

The gaseous contents of the chamber were introduced directly in to the mass spectrometer and the mass spectrum obtained. The results are summarized in Table 1.

### *5.3. Auger electron spectroscopic analysis of film photoproduced from a Ti(acac)$_2$(i-prop)$_2$ film*

A Ti(acac)$_2$(*i*-prop)$_2$ precursor film was prepared as described in Section 5.2. The film was then irradiated under the UV light for 4 h. An FTIR spectrum of the film was obtained confirming complete loss of vibrations associated with the ligands. The sample was then moved to the Auger electron spectrometer for analysis. The results are summarized in Table 2.

### *5.4. Thermal treatment of films produced by the photolysis of films of Ti(acac)$_2$(i-prop)$_2$*

A Ti(acac)$_2$(*i*-prop)$_2$ precursor film was prepared as described in Section 5.2. The film was irradiated under the UV light for 4 h. The photoproduced film on the silicon chip was heated at 300 °C in an oven for 2 h. An XRD spectrum was obtained after heating. The preparation of the other samples was similar to the one described in previous sections. The amorphous films were obtained from the photolysis of Ti(acac)$_2$(*i*-prop)$_2$ precursor films. The films were heated at temperatures of 500, 700, 900 and 1100 °C, respectively in an oven for 2 h. The XRD spectrum was obtained following the heat treatment. The results are shown in Fig. 3.

## Acknowledgements

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