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Photolithography of amorphous films of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ on silicon (111) resulting in TiO_2: the mechanism of the photodeposition reaction

B. J. PALMER, A. BECALSKA, T. W. H. HO, R. H. HILL
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Photolithography to produce TiO_2 patterns from amorphous films of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ has been demonstrated. The efficiency of the reaction has been measured yielding a quantum yield of 0.025. The mechanism of the photoreactions of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ has been studied using Fourier transform–infrared spectroscopy in both a low-temperature 1,2-epoxyethylbenzene glass and as surface films. In each case the primary photochemical process was found to be loss of a single azido group. The result of subsequent photolysis was found to be dependent upon medium and temperature. In the low-temperature glass no further photochemistry was observed. The exhaustive photolysis of films at 20 K, or room temperature, under a vacuum or in air led to loss of all ligands and the formation of TiO_2.

1. Introduction

The deposition of metal, metal oxide and metal nitride films on surfaces has attracted a great deal of interest recently due to their importance in the semiconductor industry. Several methods have been used including sol–gel, plasma techniques, chemical vapour deposition, and photochemical deposition [1–4]. Each of these methods has advantages, and the latter two have the advantage of low process temperatures. Additionally, the photochemical methods allow for beam-directed deposition of the desired film, simplifying the overall process methodology [5].

In spite of the apparent low temperatures of the photochemical process in many systems the deposition process is not truly photochemical but the result of a photon-energized thermal process. This is often the predominant mode of reaction following an initial photochemical step. The initial photon may lead to facile loss of a ligand and cause the molecule to adhere to the substrate. Further decomposition is the result of thermolysis of the surface-bound species [6, 7]. If the surface reactions could be induced in a true photochemical process then the local process temperature would also be reduced. Such low temperatures would be advantageous in the fabrication of multilevel VLSI devices. There is, however, little known about the photochemistry of organometallic complexes on surfaces. We have initiated a study of films on surfaces with the goal of identifying facile photochemical reactions which may be induced at low temperatures [8].

In this study we demonstrate, not only the possibility of an entirely photochemical deposition process, but also that the deposition may be carried out entirely in the solid amorphous phase. This results in a low-energy deposition process which is also compatible with current lithography methods.

In this study we chose to observe $(\eta^5\text{-}C_5H_5)_2\text{-}Ti(N_3)_2$ for a number of reasons. The complex is involatile allowing for the study of the surface photochemistry in a vacuum. Secondly, the azido group is known to be photosensitive and may ultimately decompose to yield either the metal or metal nitrides. It should be noted that both loss of nitrogen from the azide ligand and loss of the azide ligand as a radical have been observed to be induced photochemically in solution [9–11]. The azido group is an intense chromophore in the infrared, allowing us to study lower surface coverages than were possible in the earlier study. The known photochemistry of Cp_2TiX_2 complexes suggests that the cyclopentadienyl ligand may also be photoextruded [12–15]. These studies suggested that the photochemistry may indeed lead to loss of all ligands and the production of TiO_2 films.

In this report we will concentrate on the photochemistry of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ leading to the production of TiO_2 films. High-quality TiO_2 films can be prepared by spray-pyrolysis methods [16–18]. Deposition of titanium films has been accomplished by laser-assisted chemical vapour deposition [19, 20]. However, the method described here is the first example of a process compatible with current mask lithography methods.

2. Experimental procedure

The complex, $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$, was prepared by literature [21] methods. The CaF_2 crystals used were obtained from Wilmad Glass Co. Inc. The Si(1 1 1)

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wafers were obtained from Pacific Microelectronics Center, Canada. The wafers were *p*-type silicon with tolerances and specifications as per SEMI Standard M1.1.STD.5. The wafers were cut to the approximate dimensions of 1 cm × 1.5 cm in house.

The 1-^{15}N sodium azide was obtained from Cambridge Isotopes and was 99 at % ^{15}N-enriched in the 1 position.

The Fourier transform–infrared (FT–IR) spectra were obtained with 4 cm^{-1} resolution using a BOMEM Michelson 120 FT–IR spectrophotometer. The samples were held either in a CaF_2-faced cell (glasses) or a high conductivity copper sample mount within a CaF_2-faced vacuum Dewar. For experiments at 20 K the samples were cooled with a CTI-Cryogenics Model 22 cryocooler attached to a Model 350R compressor system. The cold head was equipped with CaF_2 optics. Temperatures were controlled and monitored with a Lake Shore Cryotronics silicon diode sensor (Model DT500 DRC) in conjunction with a Model DRC 80C temperature controller.

The photolysis beam was a 100 W high-pressure mercury lamp in an Oriel housing equipped with condenser lenses and filtered through a 10 cm water filter with Pyrex optics.

X-ray photoelectron spectra were obtained using a PHI double pass CMA at 0.85 eV resolution at the Surface Physics Laboratory, Department of Physics, Simon Fraser University. The depth profile was obtained by sputtering with Ar^+ at 3 keV.

2.1. Preparation of $(^{15}N)_2$-labelled $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$

To a solution containing $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (0.04 g) in acetone (20 ml) solid 1-$Na^{15}NN_2$ (0.01 g) was added. The mixture was stirred for 24 h. The solvent was then removed under reduced pressure and the solid extracted with CH_2Cl_2 which, after removal, yielded $(^{15}N)_2$-$(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$, 0.032 g, 77%.

2.2. Photolysis of complexes in a 1,2-epoxyethylbenzene glass

A sample of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ was dissolved in 1,2-epoxyethylbenzene and loaded into a CaF_2-faced cell. The sample was then cooled to 77 K and the FT–IR spectrum obtained. The sample was then irradiated for 20, 30, 37, 60 and 120 min.

Similar experiments were conducted at 20 K utilizing the cryocooler system.

2.3. Calibration of absorption on a surface

A stock solution of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ (0.0060 g) was prepared in CH_2Cl_2 (9.0 ml). A drop (0.0031 ml) of this solution was then deposited on the surface of a silicon wafer, allowed to evaporate, and the absorbance measured (Fig. 1a). The area of the drop was found to be 0.5 cm^2. This corresponds to a coverage of 0.94 × 10^2 molecules/nm^2. This process was repeated several times. A calibration curve for absorbance versus moles of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ deposited is shown in Fig. 1b.

2.4. Photolysis of complexes on silicon surfaces

For photolysis, a silicon surface was prepared with $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ as above and transferred to the vacuum Dewar. This was then photolysed for 30, 60, 90, 120 s and 3, 8, 35, 72, 102 and 1182 min. Spectral changes are summarized in Figs 2 and 3.

Similar experiments were done at 77 K by cooling the vacuum Dewar with liquid nitrogen. Experiments at 20 K were done using the cryocooler.

Alternate experiments were done in which the sample was deposited on the surface by spin coating. In this method a drop of a $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ solution (in CH_2Cl_2) was dropped on to a spinning silicon chip. The resultant surface was typically found to be covered with 60 monolayers. The sample was then photolysed as above.

2.5. Quantum yield measurements

A sample of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ on a silicon chip was prepared by the spin-coating method. This sample was transferred to the vacuum Dewar which was then evacuated. The sample was then irradiated with the filtered (λ = 366 nm) output of the mercury lamp and monitored by FT–IR. The incident intensity of the light source was measured to be 7.5 mW. The intensity of the 2084 cm^{-1} band was found to decrease with photolysis time and a plot of $\ln(A_0/A_t)$ versus incident light (J) is shown in Fig. 4.

A similar experiment in which the sample chamber was left open to the air was also conducted. The results of this experiment are reported in Fig. 5.

In each case the filter system results in the transmission of the 366 nm line of the mercury lamp. The extinction coefficient for the complex is estimated from the solution spectra to be 1.7 × 10^6 cm^2 mol^{-1}. The initial absorbance at the irradiation wavelength is calculated from the extinction coefficient and the coverage. The quantum yield in each case is then given by Equation 1. For the photolysis of a $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ film under vacuum the values of

$$\Phi = \{-(\phi)[N/(I_0)(A(0))]\} \qquad (1)$$

where Φ is the quantum yield, N the total number of moles complex deposited on the surface, ϕ the slope of a plot of $\ln(A(0)/A(t))$ versus the work of light (mJ), where, $A(0)$ is the absorbance at time = 0 and $A(t)$ is the absorbance at time t, I_0 is the intensity of the incident light (mW), and $A(0)$ is the absorbance of the film at time zero based on the solution extinction coefficient at 366 nm. ϕ, I_0 and $A(0)$ are 4.24×10^{-4} s^{-1}, 2.29×10^{-8} einstein s^{-1}, and 7.35×10^{-2} cm^2 mol^{-1} (for the 2084 cm^{-1} band), respectively. For the photolysis of an $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ film in air the values of ϕ, I_0, and $A(0)$ are 2.14×10^{-4} s^{-1}, 2.29×10^{-8} einstein s^{-1}, and 7.20×10^{-2} cm^2 mol^{-1}, respectively. The total number of moles photolysed in vacuum and in air was 2.13×10^{-8} and 2.29×10^{-8},

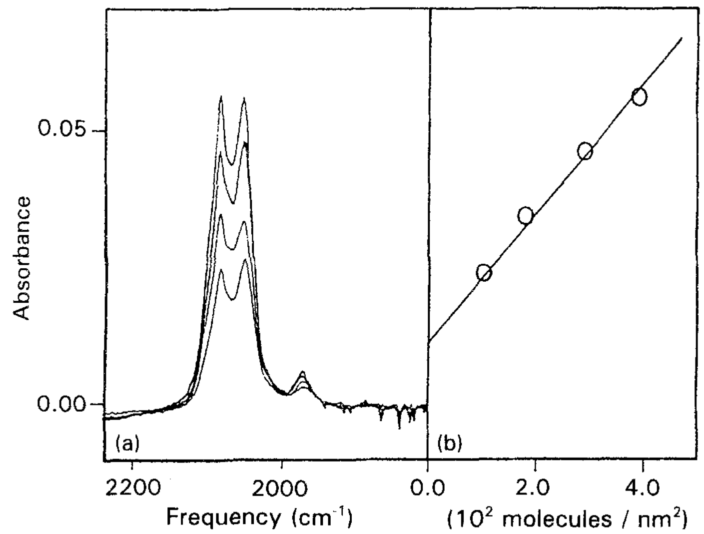

Figure 1 (a) FT–IR spectra associated with 0.9×10^2, 1.8×10^2, 2.8×10^2 and 3.7×10^2 molecules of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ per nm^2 on a silicon surface. (b) Plot of absorbance of the high-energy component of the antisymmetric N_3 stretch of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ versus coverage, data from (a).

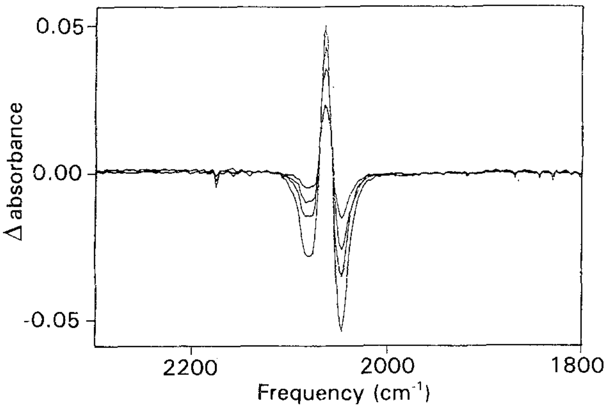

Figure 2 FT–IR spectral changes associated with the photolysis of a film of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ on a silicon surface for 30, 60, 90 and 120 s.

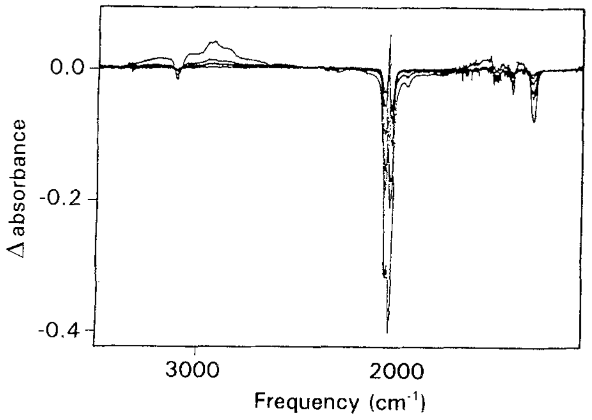

Figure 3 FT–IR spectral changes associated with the photolysis of a film of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ on a silicon surface for 3, 8, 35, 72, 102 and 1182 min.

respectively. The quantum yield determined for the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ under vacuum is 0.005. The quantum yield determined for the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ under an air atmosphere is 0.025.

3. Results and discussion

3.1. Spectroscopic data for the complexes

The optical absorption spectra of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ consist of a number of bands, probably all charge transfer in nature. The spectra in different solvents are given in Table I. The first transition is near 400 nm (extinction coefficient about 2000–5000 $M^{-1}\,cm^{-1}$). At higher energy a much more intense band is observed. The higher energy band has an extinction coefficient on the order of 20000 $M^{-1}\,cm^{-1}$ and is associated with a charge transfer transition. The band at 400 nm has been reported previously [16, 17].

As part of a study of the photochemistry of other derivatives, $(\eta^5\text{-}C_5H_5)_2TiX_2$ X = Cl, Br, I, Me, the spectra of these have been discussed. They are similar to X = N_3 observed here [12, 13].

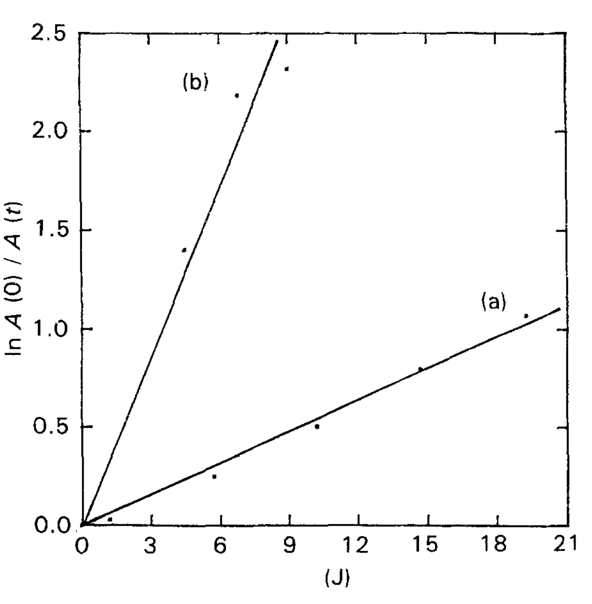

Figure 4 (a) Plot of $\ln(A_0/A_t)$ versus incident light (mJ) for the loss of the 2084 cm^{-1} band of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ photolysed *in vacuo*. (b) Plot of $\ln(A_0/A_t)$ versus incident light (J) for the loss of the 2084 cm^{-1} band of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ photolysed in air.

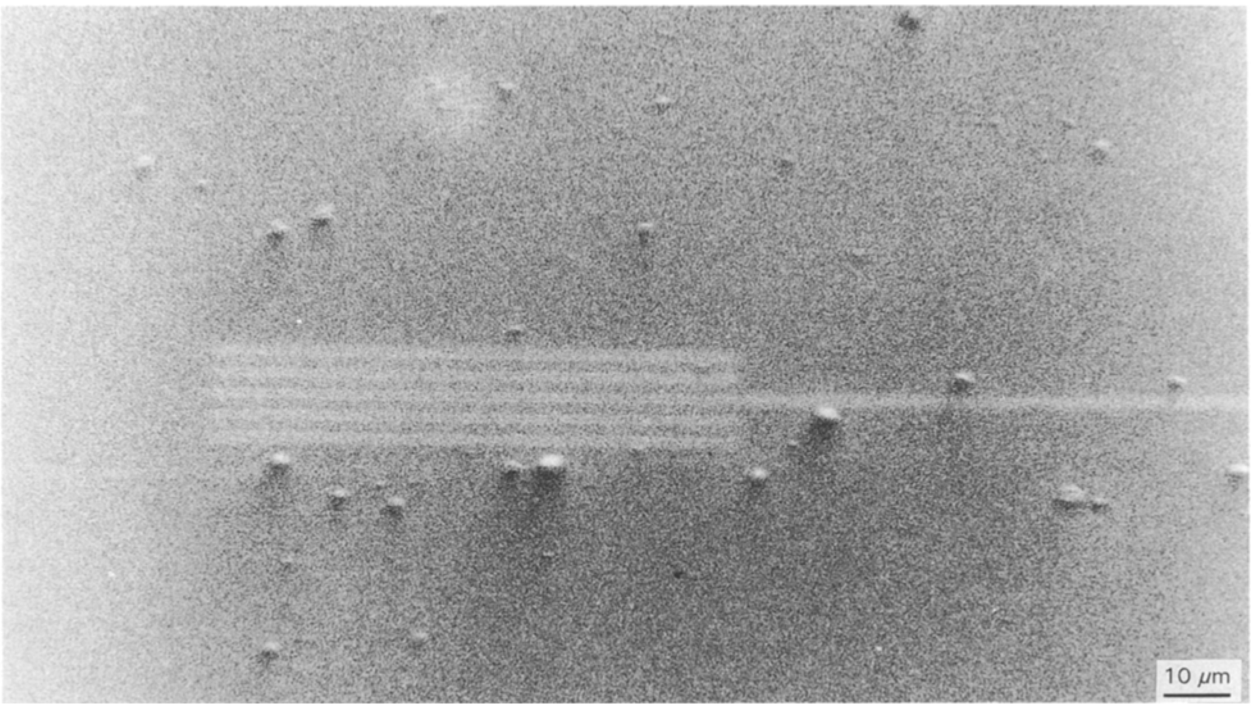

Figure 5 Scanning electron micrograph of TiO_2 deposited from a film of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ by photolysis through a mask.

TABLE I Optical data for $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$

Solvent	Wavelength (nm)	Extinction coefficient ln $(M^{-1}\,cm^{-1})$[a]
Acetone	408	8.3
Toluene	412	8.5
	290	9.7
Ethanol[b]	404	7.7
	280	9.5
Ether	412	8.2
	288	9.4
$CHCl_3$	408	8.2
	284	9.9

[a] Owing to the decomposition of these solutions the extinction coefficients presented here are approximate.

[b] In this case the decomposition was so significant that the wavelengths are approximate.

The photochemistry observed here is a result of photolysis of the low-energy transition. It is consistent with an azide to metal charge transfer band. Photolysis at higher energy, using unfiltered light, resulted in no change in the observed photochemistry consistent with rapid internal conversion to the lowest excited state.

The FT–IR spectrum of the antisymmetric stretch of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ on a silicon surface is shown in Fig. 1a. Note that little change in appearance is observed over a coverage range from 0.9×10^2–4×10^2 molecules nm^2. The linear nature of the plot, Fig. 1b, indicates that there is no detectable thermal chemistry occurring upon deposition. It should also be noted that the invariance of the absorption spectra with coverage are consistent with the thickness of the film being utilized in this study. In each case the coverages are several monolayers thick, hence the observed absorption is due to a *bulk* film. The interfacial layer, at either the silicon or vacuum interface, is not making a significant contribution to the observed spectra. The silicon surface is not terminated by silicon but rather by an oxide layer the surface of which is thought to terminate in hydroxy groups. This coverage is in the region required for technically useful films [22].

The FT–IR spectra for $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$, its ^{15}N-labelled derivative and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ are summarized in Table II. The most intense peaks in the IR spectra of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ are those associated with the antisymmetric azide stretches which appear at 2084 and 2051 cm^{-1}. The symmetric band is observed at 1348 cm^{-1} and is split by 10 cm^{-1}. This agrees with the literature assignment [23]. These bands shift to lower energy in the $(\eta^5\text{-}C_5H_5)_2Ti(^{15}NN_2)_2$ derivative. It must be noted that the labelled complex represents a mixture of the following isotopomers; $(\eta^5\text{-}C_5H_5)_2Ti(^{15}N^{14}N_2)_2$, $(\eta^5\text{-}C_5H_5)_2Ti(^{14}N_2\,^{15}N)_2$ and $(\eta^5\text{-}C_5H_5)_2Ti(^{14}N_2\,^{15}N)(^{15}N^{14}N_2)$ in the ratio of 1:1:2. Owing to the three different isotopomers being observed, the antisymmetric stretches are broadened and we observe a superposition of the three spectra. Similar mixtures have been observed previously in mono-azido compounds [24, 25]. The symmetric band shifts 25 cm^{-1} to lower energy in the labelled complex; however, no evidence for fine structure is observed. A similar result is found upon labelling surface-bound NaN_3.

In addition to these bands, both CC and CH absorptions are present and are summarized in Table II. These are assigned by analogy to the CH and CC modes for $(\eta^5\text{-}C_5H_5)_2TiCl_2$ which have been reported by others [26–28]. The spectral data for $(\eta^5\text{-}C_5H_5)_2TiCl_2$ deposited on a silicon surface are included in Table II and are not significantly different from those in other media.

TABLE II FT–IR spectral data for relevant complexes

Complex	Medium	νa (N_3) (cm^{-1})	νs (N_3) (cm^{-1})	ν (CH) (cm^{-1})	ν (CC) (cm^{-1})
$(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$	Surface	2084, 2051	1348	3106	1443
	Glass	2077, 2049			
$^{15}N_2\text{-}(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$	Surface	2063, 2039	1315	3106	1443
	Glass	2068, 2036			
$(\eta^5\text{-}C_5H_5)_2Ti(N_3)$	Surface	2077	1333	3107	1446
	Glass	2069			
$^{15}N_2\text{-}(\eta^5\text{-}C_5H_5)_2Ti(N_3)$	Surface	2063	1311	3107	1446
	Glass	2066			
$(\eta^5\text{-}C_5H_5)_2Ti(Cl)_2$	Surface			3105	1440

3.2. Photochemistry of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ in a low-temperature glass

Before discussion of the results obtained in a film, we will describe the results found in a 1,2-epoxyethylbenzene glass. Photolysis was conducted at 77 K where 1,2-epoxyethylbenzene forms a transparent glass. The initial result of photolysis was loss of intensity due to the azide antisymmetric absorptions at 2077 and 2049 cm^{-1}. Concomitant growth of a new absorption at 2069 cm^{-1} was observed. Both the absorption due to the starting complex and the product shifted upon ^{15}N-labelling of the complex. This indicated that the product absorption is due to an azide. The spectral changes are consistent with loss of a single azide ligand and formation of $(\eta^5\text{-}C_5H_5)_2TiN_3$. The reaction is as shown in Equation 2.

$$(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)_2Ti(N_3) + N_3 \qquad (2)$$

This overall result is obtained at either 77 or 20 K and the photoreaction may be achieved with filtered (bandpass > 400 nm or bandpass > 480 nm) light or the unfiltered output of a mercury lamp. The fate of the azide ligand is not clear. Possible decomposition to N_2 may occur although we observed no absorption bands attributable to either the radical [29–31], N_3, or free $N^{15}N$ [32]. (Note that $^{15}N^{14}N$ is expected to have a very low extinction coefficient and has not been observed in the infrared.)

Prolonged photolysis leads to no further photoreaction on a reasonable timescale. For example, one sample was photolysed for more than 6 days at 20 K (3 days with bandpass > 480 nm and a further 3 days with only a water filter) and no degradation of the primary photoproduct, $(\eta^5\text{-}C_5H_5)_2TiN_3$, was observed. This indicates a much lower photosensitivity in a glass than is described below for a film.

3.3. Photochemistry of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ as a film

Room-temperature photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ results in the initial loss of the antisymmetric stretches of the azides and the appearance of a new band. This is illustrated in Fig. 2. The new band which is within the envelope of the absorptions due to the starting material may be seen clearly by computer addition of the starting material absorption. Under these conditions the correct band position is identified as 2077 cm^{-1}. Upon ^{15}N labelling of the starting complex this product absorption shifts to lower energy, appearing at 2063 cm^{-1} and is considerably broadened (half-width 50 cm^{-1} compared to 30 cm^{-1} for the unlabelled derivative). The photoreaction is as shown in Equation 2. The broad band in the absorption due to the substituted complex is consistent with the formation of the two isotopomers, $(\eta^5\text{-}C_5H_5)_2Ti(^{15}NN_2)$ and $(\eta^5\text{-}C_5H_5)_2Ti(N_2{}^{15}N)$. No other changes were observed in the spectrum of this system in the initial stages of photolysis. Importantly, no new peaks were observed in the region of 1000 cm^{-1} which would indicate a nitrido ligand. We hence formulate the reaction as occurring via loss of the azido radical which subsequently decomposes to generate N_2.

The other spectral regions appear to remain unperturbed by this process. This initial reaction we assign as due to loss of a single azide ligand. Even at 20 K where the loss of azide is readily apparent we see no definitive peaks attributable to N_3 radical formation [29–31] or to N^{15} N formation [32]. This may be due to its ready decomposition in the presence of titanium. Broad peaks were observed in the region of 1600 cm^{-1} although these were weak. The photolysis at either 77 or 20 K shows an additional feature in the FT–IR spectra. The antisymmetric azide stretch is split with a component at higher energy. This band which appears as a shoulder shifts upon ^{15}N substitution and is probably associated with a rotomer of the remaining azide ligand.

Prolonged photolysis of this sample results in the spectral changes shown in Fig. 3. Loss of the $(\eta^5\text{-}C_5H_5)_2Ti(N_3)$ complex is indicated by loss of all absorptions due to the azide ligand, both antisymmetric and symmetric bands, and loss of the absorptions due to coordinated $(\eta^5\text{-}C_5H_5)$. The only new absorptions observed in this process are in the region of 3000 and 1600 cm^{-1}. These bands are unshifted in the ^{15}N-labelled species and are associated with the fragments derived from the uncoordinated (C_5H_5).

Samples prepared by spin coating of a silicon chip were somewhat thinner and more uniform. Typically we were able to prepare films ~120 nm thick by this

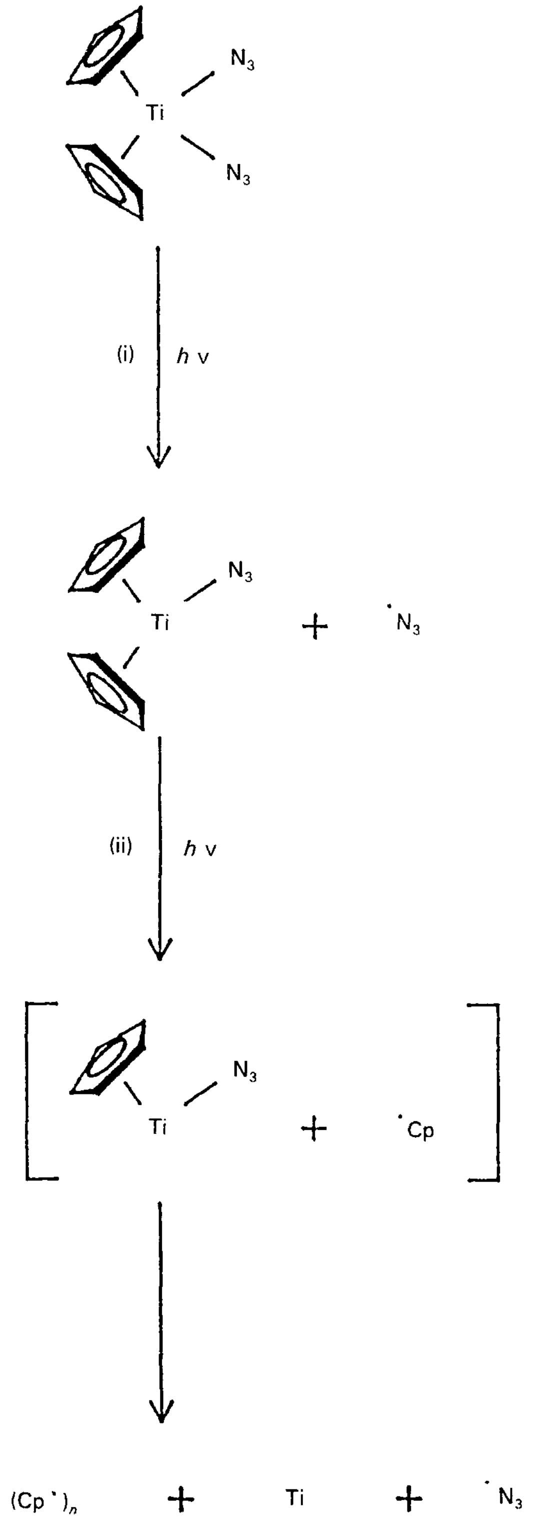

Figure 6 (i) Photolysis in a glass at either 77 or 20 K, or photolysis in a film at either 300, 77 or 20 K. (ii) Photolysis in a film at 300, 77 or 20 K.

method. The spectral changes associated with photolysis of these films at room temperature are consistent with those above, although these thin films show no evidence of hydrocarbon product in the IR spectra following prolonged photolysis. This presumably is due to the loss of products derived from (C_5H_5) to the vacuum.

Repetition of the above photolysis using wavelengths longer than 420 nm has no effect upon the observed spectral changes. For comparison with the lack of photosensitivity observed in the glass it should be noted that a film held at 20 K and photolysed for 18 h shows loss of 75% of the (η^5-$C_5H_5)_2Ti(N_3)$.

If the photolysis of a film is conducted under an air atmosphere the above-mentioned intermediate is not observed. Loss of all absorptions in the infrared occurs with no peaks attributable to (η^5-$C_5H_5)_2Ti(N_3)$ being observed.

The final films, resultant after prolonged photolysis, were removed and transferred to the X-ray photoelectron spectrometer. The results depended upon the method of preparation of the initial amorphous film of (η^5-$C_5H_5)_2Ti(N_3)_2$. When films were prepared by spin coating the wafer the only significant peaks observed in the Auger were indicative of carbon (38%) titanium (23%) and oxygen (39%). Both the relative amounts of titanium and oxygen and the position of the titanium lines $2p_{3/2}$ at 558.2 and $2p_{1/2}$ at 562.8 eV are indicative of TiO_2 formation. The carbon is presumably present as organic contamination of the surface. Sputtering the surface with argon ions for 30 s results in a decrease in the carbon signal to $\sim$10% and a change in the titanium oxygen stoichiometry to TiO. This behaviour is consistent with the observed apparent reduction of TiO_2 upon sputtering [33]. This result indicates that the film is a homogeneous TiO_2 layer rather than a mixture of oxides. At longer sputtering times, a much slower loss of carbon was observed but this signal did not fall to baseline levels until silicon was the most intense spectral signal. At this point the signal due to titanium was approximately half that due to silicon. The carbon content of the film is probably a result of contamination rather than inefficient photochemistry. Unfortunately we are not able to transfer the surfaces from the photolysis chamber to the Auger spectrometer without exposing them to air.

One further feature of the Auger spectra is of significance. The initial appearance of a peak due to silicon, following sputtering, was associated with metallic silicon rather than SiO_2 in spite of the fact that the wafers were not subjected to an HF etch. The native oxide layer presumably is, at least in part, the source of oxygen for the formation of TiO_2. This reaction results in the formation of a native silicon layer.

Films prepared by evaporation of a solution containing (η^5-$C_5H_5)_2Ti(N_3)_2$ were also analysed by Auger spectroscopy. The formation of TiO_2 was also observed in these films. The films contained much larger amounts of carbon (approximately 15 times as abundant as titanium) and measurable concentrations of nitrogen. A slight asymmetry exists in the titanium lines indicating the possible formation of TiN. The photoelectron signals due to the N 1s line consists of two peaks at 398 and 399.4 eV, indicative of the formation of organic nitrogen-containing species and possibly some TiN. We can estimate from this the maximum amount of TiN to be less than 20%. From the appearance of the titanium line this probably provides an over estimate. The films prepared this way were not uniform as attested to by the initial observation of peaks attributable to silicon (both SiO_2 and Si) prior to sputtering the surface.

Surface Raman spectra were obtained with the aim of identifying if the TiO_2 was anatase or rutile. No signals associated with TiO_2 were observable due to intense emission from the organic by-products. Repeated rinsing of the surface with a variety of solvents did not remove this contaminant. We interpret this as evidence for the formation of a polymeric material derived from uncoordinated (C_5H_5).

Our interpretation is that the primary photoproduct, $(\eta^5\text{-}C_5H_5)_2TiN_3$, loses all ligands and generates titanium metal which is then oxidized. Depending on conditions, the source of oxygen is either the SiO_2 surface or the atmosphere. The initial result of photolysis of $(\eta^5\text{-}C_5H_5)_2TiN_3$ is presumably (C_5H_5) loss. Loss of N_3 would be expected to result in the formation of products of the formula $(\eta^5\text{-}C_5H_5)_2Ti$ and our observed IR spectrum is inconsistent with these products [34]. It is notable that a form of $(\eta^5\text{-}C_5H_5)_2Ti$ may be produced photochemically from $(\eta^5\text{-}C_5H_5)_2TiMe_2$ indicating that, at least in solution, this product is photostable [35]. That we do not observe this product indicates an alternate photoprocess is occurring. Lastly, the observed FT–IR has the same absorption positions as was observed to result from the photodecomposition of $(\eta^5\text{-}C_5H_5)Mn(NO)(CO)_2^+$ in a film [8] indicating the production of uncoordinated (C_5H_5).

It should be pointed out that the second photoreaction, loss of (C_5H_5), has been invoked in the photochemistry of $(\eta^5\text{-}C_5H_5)_2TiCl_2$. Although we apparently do not observe this reaction in the case of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ we do observe this for $(\eta^5\text{-}C_5H_5)_2TiN_3$. This difference may be due to the phase we are studying where both in glass and in the film (C_5H_5) radicals could not diffuse away from the titanium, hence no reaction would be observed. The study of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ was conducted in solution where diffusion of the radical could occur. Here the $(\eta^5\text{-}C_5H_5)TiN_3$ formed upon loss of $(\eta^5\text{-}C_5H_5)$ from $(\eta^5\text{-}C_5H_5)_2TiN_3$ must readily decompose, preventing the reverse reaction with the (C_5H_5) radical.

The titanium, once formed, then reacts with oxygen, from either SiO_2 or the vacuum, to produce the resultant TiO_2. The vacuum used in these experiments was of the order of 10^{-3} torr (1 torr = 133.322 Pa). Under these conditions it is also possible that photolysis of $(\eta^5\text{-}C_5H_5)_2TiN_3$ results in the formation of an intermediate which reacts with oxygen to form TiO_2 without the intermediacy of titanium metal. This seems unlikely as $(\eta^5\text{-}C_5H_5)_2TiN_3$ which is also air sensitive is readily observed under this vacuum.

An approximate measure of the quantum yield for the process was obtained by photolysis with 366 nm light. The relative photosensitivity, in vacuum and under an atmosphere of air, is shown in Fig. 4. Irradiation under vacuum led to an approximate quantum yield for the process of 0.005. In air, where the $(\eta^5\text{-}C_5H_5)_2TiN_3$ reacts thermally with oxygen, the decomposition quantum yield was 0.025. To show that this result was indeed a result of oxygen in the air, the quantum yield was also measured in nitrogen, containing some air, and found to be 0.01. This result is consistent with the varying stability of $(\eta^5\text{-}C_5H_5)_2TiN_3$ under these conditions. In a vacuum, $(\eta^5\text{-}C_5H_5)_2TiN_3$ is stable and requires more light for its photochemical decomposition, resulting in a lower overall decomposition quantum yield. In air, $(\eta^5\text{-}C_5H_5)_2TiN_3$ is not stable, undergoing thermal reactions with oxygen. The quantum yield measured here is a reflection of the initial photoreaction of $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$ which, under these conditions, is the only photoreaction.

The results indicate that this system should be amenable to processing by standard lithographic methods. In order to test this, a sample prepared by spin coating of a silicon chip, was photolysed under a mask in contact with the wafer. The sample was then washed with CH_2Cl_2, to remove unexposed $(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$, and imaged by a SEM to yield the pattern shown in Fig. 5. The pattern, five lines with one twice as long as the remaining four, is clearly visible. In this case the lines are ~2 μm wide. This result demonstrates that this chemistry is compatible with standard lithographic procedures.

4. Conclusions

The results of photolysis under different conditions are summarized in the scheme. In a film, loss of all ligands may be induced photochemically at temperatures as low as 20 K. This has been demonstrated with very weak photon fluxes which indicate that the reaction is not dependent on thermal heating of the surface. We have demonstrated that TiO_2, which is useful as a dielectric in VLSI devices [36], could be formed in a photochemical process at temperatures of 20 K.

Of primary importance in this study is the indication that lithography to generate metal and metal oxide patterns on semiconductors may not require the use of polymer films. Direct lithography of films composed of inorganic and organometallic materials provides an alternate route to the production of metal and metal oxide patterns. Within this context, further work is required to investigate the electrical properties and obtainable purity of the films produced in this manner.

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References

1. M. J. ALMOND, D. A. RICE and C. A. YATES, *Chem. Brit.* **24** (1988) 1130.
2. K. KOHNO, *J. Mater. Sci.* **27** (1992) 658.
3. M. R. KOZLOWSKI, P. S. TYLER, W. H. SMYRL and R. T. ATANASOSKI, *J. Electrochem. Soc.* **136** (1989) 442.
4. K. A. SINGMASTER, F. A. HOULE and R. J. WILSON, *Appl. Phys. Lett.* **53** (1988) 1048.
5. H. H. GILGEN, T. CACOURIS, P. S. SHAW, R. R. KRCHNAVEK and R. M. OSGOOD, *Appl. Phys. B* **42** (1987) 55.

6. N. S. GLUCK, Z. YING, C. E. BARTOSCH and W. HO, *J. Chem. Phys.* **86** (1987) 4957.
7. I. P. HERMAN, *Chem. Rev.* **89** (1989) 1323.
8. B. J. PALMER, A. BECALSKA and R. H. HILL, *J. Photochem. Photobiol. A Chem.* **57** (1991) 457.
9. J. L. REED, F. WANG and F. BASOLO, *J. Amer. Chem. Soc.* **94** (1972) 7137.
10. C. BARTOCCI and F. SCANDOLA, *J. Chem. Soc. Chem. Commun.* (1970) 531.
11. J. F. ENDICOTT, M. Z. HOFFMAN and L. S. BERES, *J. Phys. Chem.* **74** (1970) 1021.
12. R. W. HARRIGAN, G. S. HAMMOND and H. B. GRAY, *J. Organomet. Chem.* **81** (1974) 79.
13. A. VLECK Jr, *ibid.* **297** (1985) 43.
14. Z. TSAI and C. H. BRUBAKER Jr, *ibid.* **166** (1979) 199.
15. M. R. M. BRUCE, A. SCLAFANI and D. R. TYLER, *Inorg. Chem.* **25** (1986) 2546.
16. W. A. BADAWY, F. DECKER and K. DOBLHOFER, *Solar Energy Mater.* **8** (1983) 363.
17. W. A. BADAWY and E. A. EL-GIAR, *Thin Solid Films* **158** (1988) 277.
18. W. W. XU, R. KERSHAW, K. DWIGHT and A. WOLD, *Mater. Res. Bull.* **25** (1990) 1385.
19. W. B. CHOU, M. N. AZER and J. MAZUMDER, *J. Appl. Phys.* **66** (1989) 191.
20. J. Y. TSAO, R. A. BECKER, D. J. EHRLICH and F. J. LEONBERGER, *Appl. Phys. Lett.* **42** (1983) 559.
21. C. H. LANGFORD and J. P. APLINGTON, *J. Organomet. Chem.* **4** (1965) 271.
22. M. J. RAND, *J. Electrochem. Soc.* **120** (1973) 686.
23. R. S. P. COUTTS and P. C. WAILES, *Austr. J. Chem.* **24** (1971) 1075.
24. D. M. KURTZ Jr, D. F. SHRIVER and I. M. KLOTZ, *J. Amer. Chem. Soc.* **98** (1976) 5033.
25. J. E. PATE, T. J. THAMANN and E. I. SOLOMON, *Spectrochim. Acta* **42A** (1986) 313.
26. P. M. DRUCE, B. M. KINGSTON, M. F. LAPPERT, T. R. SPALDING and R. C. SRIVASTAVA, *J. Chem. Soc. A* (1969) 2106.
27. E. SAMUEL, R. FERNER and M. BIGORGNE, *Inorg. Chem.* **12** (1973) 881.
28. G. BALDUCCI, L. BENCIVENNI, G. DE ROSA, R. GIGLI, B. MARTINI and S. N. CESARO, *J. Molec. Struct.* **64** (1980) 163.
29. J. I. BRYANT, *Spectrochim. Acta* **22** (1966) 1475.
30. R. TIAN, J. C. FACELLI and J. MICHL, *J. Phys. Chem.* **92** (1988) 4073.
31. C. R. BRAZIER, P. F. BERNATH, J. B. BURKHOLDER and C. J. HOWARD, *J. Chem. Phys.* **89** (1988) 1762.
32. S. PINCHAS and I. LAULICHT, "Infrared Spectra of Labelled Compounds" (Academic Press, London, 1971).
33. J. GANDON and J. C. JOUD, *J. Less-Common Metals* **69** (1980) 277.
34. J. E. BERCAW, R. H. MARVICH, L. G. BELL and H. H. BRINTZINGER, *J. Amer. Chem. Soc.* **94** (1972) 1219.
35. M. D. RAUSCH, W. H. BOON and H. G. ALT, *J. Organomet. Chem.* **141** (1977) 299.
36. R. SINGH, *Amer. Inst. Phys. Conf. Proc.* **138** (1986) 289.

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