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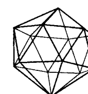
Polyhedron 22 (2003) 1263–1269



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Atmospheric pressure chemical vapour deposition of TiS_2 thin films on glass

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Received 1 November 2002; accepted 31 January 2003

Abstract

Atmospheric pressure chemical vapour deposition (APCVD) of TiS_2 films on glass substrates was achieved by reaction of $HS(CH_2)_2SH$, $HSC(CH_3)_3$ and $S(Si(CH_3)_3)_2$ with $TiCl_4$ at 275–600 °C. At substrate temperatures from 275 to 400 °C, the TiS_2 films were X-ray amorphous or nanocrystalline. At 500 °C and above, the films were crystalline with typical cell constants of $a = 3.405$ Å, $c = 5.609$ Å. All the films showed a TiS_2 Raman pattern with bands at 335 and 380 cm^{-1}. Energy-dispersive analysis by X-rays (EDAX) gave a Ti:S ratio of 1:2. The TiS_2 films were gold, highly reflective and showed semi-metal electrical conductivities. Scanning electron microscopy (SEM) showed a dense particulate morphology at low substrate temperatures (200–400 °C) and a needle-like mosaic at higher deposition temperatures. APCVD reaction of $TiCl_4$ and $(CH_3)_3C–S–S–C(CH_3)_3$ at substrate temperatures of 250–400 °C produced TiS_3 and at 500–600 °C TiS_2 films. The TiS_3 films gave Raman bands at 557, 369, 297 and 172 cm^{-1}, and a Ti:S ratio of 1:3 by EDAX.
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Keywords: Atmospheric pressure chemical vapour deposition; TiS_2; Energy-dispersive X-ray analysis

1. Introduction

Early transition metal dichalcogenides exhibit a layer structure with weak Van der Waals interactions between adjacent sulfur layers [1]. TiS_2 is particularly suitable as a cathode material as it is a semi-metal, has a high energy of formation for the lithium intercalate and can perform more than 1000 intercalation/deintercalation cycles before the charging capacity of the battery is seriously affected [2]. To maximise diffusion of the lithium ions into TiS_2, a large surface area is required such as in a thin film or fine powder form. This in turn will effect the current density produced by the battery. Use of stoichiometric TiS_2 is imperative for battery use as metal rich titanium sulfide has titanium located in the Van der Waals gap which can pin layers together and reduce the ability to intercalate [3]. Other applications of TiS_2 include uses as solid state lubricants in space-borne applications and as hydrogenation catalysts [4]. TiS_2 has an extremely attractive gold hue.

Conventionally stoichiometric ($Ti_{1.002 \pm 0.001}S_2$) titanium disulfide has been prepared from the elements by heating at temperatures up to 640 °C in a sealed evacuated ampoule with intermediate addition of excess sulfur [5]. This procedure takes 2 weeks to complete and control of product particle size is extremely difficult. Solution phase syntheses of titanium disulfide have been investigated using a variety of sulfur sources. Crystalline TiS_2 was prepared from H_2S and $TiCl_4$ at temperatures above 480 °C [6]. Formation of TiS_2 from reaction of $TiCl_4$ and hexamethyldisilathiane in solution has also been reported although the products were poorly characterised [7]. Films of titanium sulfides have been prepared from $TiCl_4$ and H_2S by plasma-enhanced chemical vapour deposition (CVD) [3], via a thio sol–gel synthesis from both titanium thiolates and alkoxides [8] and by single-source CVD from $Ti(S^tBu)_4$ [9]. Some low-pressure CVD work has been achieved using thiols and hexamethyldisilithiane [3,10]. This showed that TiS_2 and TiS_3 films can be laid down on a range of substrates at 250–500 °C [11].

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doi:10.1016/S0277-5387(03)00067-6

In this paper, we present the first atmospheric pressure CVD of TiS_2 and TiS_3 thin films from $TiCl_4$ and a range of sulfur sources: 1,2-ethanedithiol, hexamethyldisilathiane, *tert*-butyl-disulfide and *tert*-butylthiol.

2. Experimental

Nitrogen (99.99%) was obtained by BOC and used as supplied. Coatings were obtained on SiCO-coated float-glass. (The SiCO coating is an amorphous barrier layer coating approximately 50 nm thick comprising Si, C and O; it prohibits diffusion of ions from the glass into the film.) Atmospheric pressure chemical vapour deposition (APCVD) experiments were conducted on 90 mm × 45 mm × 4 mm pieces of glass using a horizontal-bed cold-wall APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (60–80 °C) and propan-2-ol and then dried in air. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. Deposition on alternative substrates (aluminium, tin oxide-coated glass and microscope slide glass) was effected by placing a 2.5 cm × 1 cm piece of the substrate on top of the usual glass substrate used. The temperature of the substrate was monitored by a Pt–Rh thermocouple. The rig was designed so that four separate gas lines could be used, all of which were made of 0.25″ diameter stainless steel, except for the inlet to the reaction chamber and the exhaust line from the reaction chamber which was 0.5″ diameter. The nitrogen carrier gas was preheated to 157 °C by being passed along 2 m lengths of coiled stainless steel tubing inside a tube furnace. Gas temperatures were monitored in situ by Pt–Rh thermocouples. Titanium (IV) chloride, $TiCl_4$ (99.9 %, Aldrich Chemical Co.), was used as supplied and placed into a stainless steel bubbler, which was heated by a heating jacket to 84 °C. $TiCl_4$ was introduced into the gas stream by passing hot N_2 through the liquid. All the sulfur sources used, namely 1,2-ethanedithiol $HS(CH_2)_2SH$, hexamethyldisilathiane $S(Si(CH_3)_3)_2$, *t*-butylthiol $HSC(CH_3)_3$ and *t*-butyldisulfide $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$ were supplied by Aldrich and used without further purification. The sulfur sources were placed in turn in a stainless steel bubbler and heated via a heating jacket ($HS(CH_2)_2SH$, 62.9 °C; $S(Si(CH_3)_3)_2$, 66.7 °C; $HSC(CH_3)_3$, 44.2 °C; $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$, 172.9 °C). The vapour produced was introduced in a stream of hot nitrogen passed through the bubbler. Flow rates of nitrogen through the bubblers was kept constant at 0.3 l min^{-1} and the flow of nitrogen make-up gas was 1 l min^{-1} for all depositions. Streams of $TiCl_4$ (diluted with nitrogen) and the sulfur source were mixed by using concentric pipes of 0.25″ and 0.5″ diameter, the inner pipe being 3 cm shorter than the outer pipe. The concentric pipes were attached directly to the mixing chamber of the coater. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with nitrogen at 150 °C for 30 min before the deposition runs. Suitable

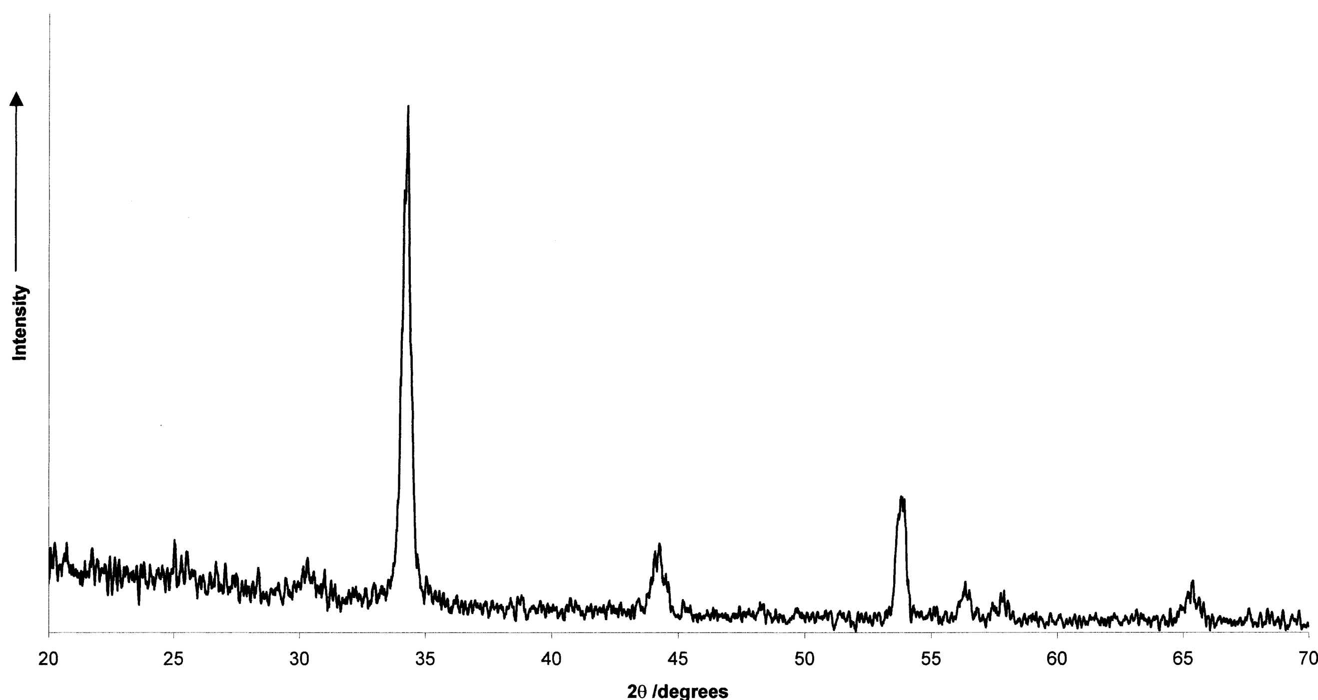


Fig. 1. X-ray powder diffraction pattern for the TiS_2 film formed on glass from the APCVD of $TiCl_4$ and $(CH_3)_3CSH$ at 550 °C.

two-way and three-way valves (rated at 200 °C) allowed the nitrogen lines to be diverted into or away from the bubbler. Deposition experiments were conducted by heating the horizontal bed reactor and the bubbler to the required temperatures before diverting the nitrogen line through the bubbler and hence to the reactor. Deposition experiments were timed by stopwatch and lasted 60 s. At the end of the deposition, the bubbler-line was closed and only nitrogen passed over the substrate. The substrate was allowed to cool with the graphite block to approximately 60 °C before it was removed. Coated substrates were handled in air and stored in a dry oxygen-free nitrogen atmosphere in a Mbraun Unilab glove box. Each system was investigated over a range of temperatures, from the onset of deposition, up to 600 °C. The films deposited on the alternative substrates were deposited at 325 °C from $TiCl_4$ and $HS(CH_2)_2SH$ only. The large substrates were cut into approximately 4 cm × 1 cm strips for analysis by SEM, XPS, Raman and UV studies. 3 cm × 2 cm strips were used for X-ray diffraction. Film adherence to the glass was assessed using the Scotch tape test and by scratching the surface using brass and steel.

X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated Cu $K\alpha_1$ radiation ($\lambda_1 = 1.5406$ Å). The diffractometer used glancing incident radiation (1.5°). Samples were indexed using Unit Cell and compared to database standards. SEM/EDAX was obtained on a Hitachi S570 instrument using the KEVEX system. UV–Vis spectra were recorded in the range 190–1100 nm using a Helios double-beam instrument. Reflectance and transmission spectra were recorded between 300 and 1200 nm by a Zeiss miniature spectrometer. Reflectance measurements were standardised relative to a rhodium mirror and transmission relative to air. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon.

The photocatalytic properties of the samples were assessed by the destruction of an overlayer of stearic acid on a 2 cm × 2 cm portion of glass. The sample was pre-irradiated for 1 h at 254 nm using a BDH germicidal lamp (2 × 8 W) prior to the addition of stearic acid. Stearic acid was applied by dropping 7.5 μl of 0.004 M stearic acid (in methanol) onto the surface of the glass. This was spun at 1500 revolutions per min to give a thin, even coverage. The coated sample was then irradiated at 15 min intervals for 1 h with intermediate measurement of the IR spectra of the stearic acid overlayer. IR measurements were carried out in the range 3000–2800 cm^{-1}. Film solubility was assessed by immersing a 2 cm × 2 cm piece of glass into solvent (acetonitrile, tetrahydrofuran, dichloromethane, ether, toluene, hexanes and concentrated nitric and hydrochloric acids).

3. Results and discussion

APCVD reactions of $TiCl_4$ and various sulfur sources $S(Si(CH_3)_3)_2$, $HS(CH_2)_2SH$, $HSC(CH_3)_3$ and $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$ were studied on glass substrates at 275–600 °C. Substrate selective studies with $HS(CH_2)_2SH$ were obtained on SnO_2 and aluminium substrates. All depositions on glass produced gold, mirror-like, highly reflective films. At deposition temperatures above 500 °C, the films had a slight brown tint. All the films passed the Scotch tape test, however they were not particularly hard as they were all scratched with a steel scalpel and brass stylus. The films were insoluble and remained unchanged on immersion in common organic solvents (THF, CH_2Cl_2, ether, hexane, toluene); however, they readily flaked off the substrate and decomposed in nitric and hydrochloric acid.

The extent of film coverage was dependent on the deposition temperature. At 275–400 °C, uniform thickness films were grown across the entire length and width of the substrate. With higher temperatures, the growth

Table 1
Raman and X-ray diffraction data for the films produced by APCVD reaction of sulfur precursors with $TiCl_4$

Substrate temperature (°C); sulfur precursor	Raman	XRD (lattice constant in Å)
275; $HS(CH_2)_2SH$	TiS_2	X-ray amorphous
300; $HS(CH_2)_2SH$	TiS_2	X-ray amorphous
325; $HS(CH_2)_2SH$	TiS_2	X-ray amorphous
350; $HS(CH_2)_2SH$	TiS_2	Nanocrystalline TiS_2
375; $HS(CH_2)_2SH$	TiS_2	Nanocrystalline TiS_2
400; $HS(CH_2)_2SH$	TiS_2	Nanocrystalline TiS_2 with preferred orientation in 0 0 2 and 1 1 0 planes
450; $HS(CH_2)_2SH$	TiS_2	Nanocrystalline TiS_2 with preferred orientation in 0 0 2 and 1 1 0 planes
500; $HS(CH_2)_2SH$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.67(2)$
550; $HS(CH_2)_2SH$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.67(2)$
400; $S(Si(CH_3)_3)_2$	TiS_2	X-ray amorphous
450; $S(Si(CH_3)_3)_2$	TiS_2	Nanocrystalline TiS_2
500; $S(Si(CH_3)_3)_2$	TiS_2	TiS_2; $a = 3.41(2)$, $c = 5.71(2)$
600; $S(Si(CH_3)_3)_2$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.84(2)$
275; $HSC(CH_3)_3$	TiS_2	X-ray amorphous
300; $HSC(CH_3)_3$	103, 231 cm^{-1}	X-ray amorphous
350; $HSC(CH_3)_3$	TiS_2	Nanocrystalline TiS_2
400; $HSC(CH_3)_3$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.71(2)$
450; $HSC(CH_3)_3$	TiS_2	TiS_2; $a = 3.41(2)$, $c = 5.67(2)$
550; $HSC(CH_3)_3$	TiS_2	TiS_2; $a = 3.41(2)$, $c = 5.68(2)$
600; $HSC(CH_3)_3$	TiS_2	TiS_2; $a = 3.41(2)$, $c = 5.70(2)$
230; $(SC(CH_3)_3)_2$	Poor spectrum 373 cm^{-1}	X-ray amorphous
250; $(SC(CH_3)_3)_2$	TiS_3	X-ray amorphous
300; $(SC(CH_3)_3)_2$	TiS_3	X-ray amorphous
350; $(SC(CH_3)_3)_2$	TiS_3	Nanocrystalline TiS_3
400; $(SC(CH_3)_3)_2$	TiS_3	Nanocrystalline TiS_3
500; $(SC(CH_3)_3)_2$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.66(2)$
550; $(SC(CH_3)_3)_2$	TiS_2	TiS_2; $a = 3.41(2)$, $c = 5.77(2)$
600; $(SC(CH_3)_3)_2$	TiS_2	TiS_2; $a = 3.40(2)$, $c = 5.71(2)$

profile was concentrated closer and closer towards the leading edge of the substrate such that at a deposition temperature of 600 °C only the first 3 cm of the substrate was coated. Thus at higher temperature, the concentration profile of the precursor along the length of the substrate is rapidly diminished as a result of fast film growth kinetics, in effect a mass transport limited regime.

Glancing angle X-ray powder diffraction of the films showed that the films grown at substrate temperatures below 300–350 °C were X-ray amorphous. Those grown at 400 °C were typically nanocrystalline TiS_2 and those grown at 450 °C and above were crystalline hexagonal TiS_2 with typical lattice constants of $a = 3.40$ Å and $c = 6.70$ Å (Fig. 1, Table 1) [12]. Some slight variation for the onset temperature for crystallinity was noted dependent on the sulfur precursor used. For $S((SiCH_3)_3)_2$, $HS(CH_2)_2SH$ and $HSC(CH_3)_3$, TiS_2 was the only phase observed; however, for $(CH_3)_3C–S–S–C(CH_3)_3$ at 400 °C nanocrystalline TiS_3 was seen (Fig. 2) [13]. At higher substrate temperatures using $(CH_3)_3C–S–S–C(CH_3)_3$ single-phase TiS_2 was identified. No substrate-selective deposition was noted at 450 °C as similar films were formed on either glass, SnO_2 or aluminium substrates using $HS(CH_2)_2SH$. The key determinant for film crystallinity was the substrate temperature. The TiS_2 films showed no obvious preferred orientation by X-ray measurements.

Raman analysis of the films grown from all different precursors and reaction temperatures showed a single phase of TiS_2 with the exception of $(CH_3)_3C–S–S–C(CH_3)_3$ at substrate temperatures from 250 to 400 °C which showed TiS_3. Notably the Raman picked up a strong signature for TiS_2 and TiS_3 even from the films that were shown to amorphous by X-ray diffraction. The Raman analysis of all the TiS_3 films showed strong bands at 557, 369, 297 and 172 cm^{-1} (Fig. 3). These and the shoulders seen in the pattern exactly match those reported by Gard et al. [14] for single-crystal TiS_3. As such all four principal bands belong to the A_g mode. The TiS_2 Raman pattern showed a strong band at 334 cm^{-1} and a shoulder at 380 cm^{-1} (Fig. 4). This maps exactly onto a reported literature spectrum of TiS_2 ($\nu =$ 335 and 380 cm^{-1}) [15]. No evidence for a secondary phase or contamination with a strong Raman scatter such as anatase was noted [16].

The reflectance/transmission spectra of all TiS_2 films showed high reflectance from 350 to 1200 nm, low transmittance from 400 to 600 nm and increasing transmittance at longer wavelengths. The crossover in reflectance/transmission properties is an important feature for a solar control coating. However, the low transmission in the visible region means that TiS_2 is largely unsuited for use in window applications. The reflectance–transmission profile for TiS_2 has been discussed in some depth in relation to semiconductor vs semi-metal behaviour [17]. The resistivity of films grown at 600 °C was approximately 400 μΩ cm. This compares to values of 1400 μΩ cm for bulk TiS_2 [18].

Scanning electron microscopy showed an interesting change in morphology with deposition temperature for all sulfur reagents. At substrate temperatures from 275 to 375 °C, a fairly dense film was formed made up of approximately 100 nm particles. At 375 and 400 °C, the

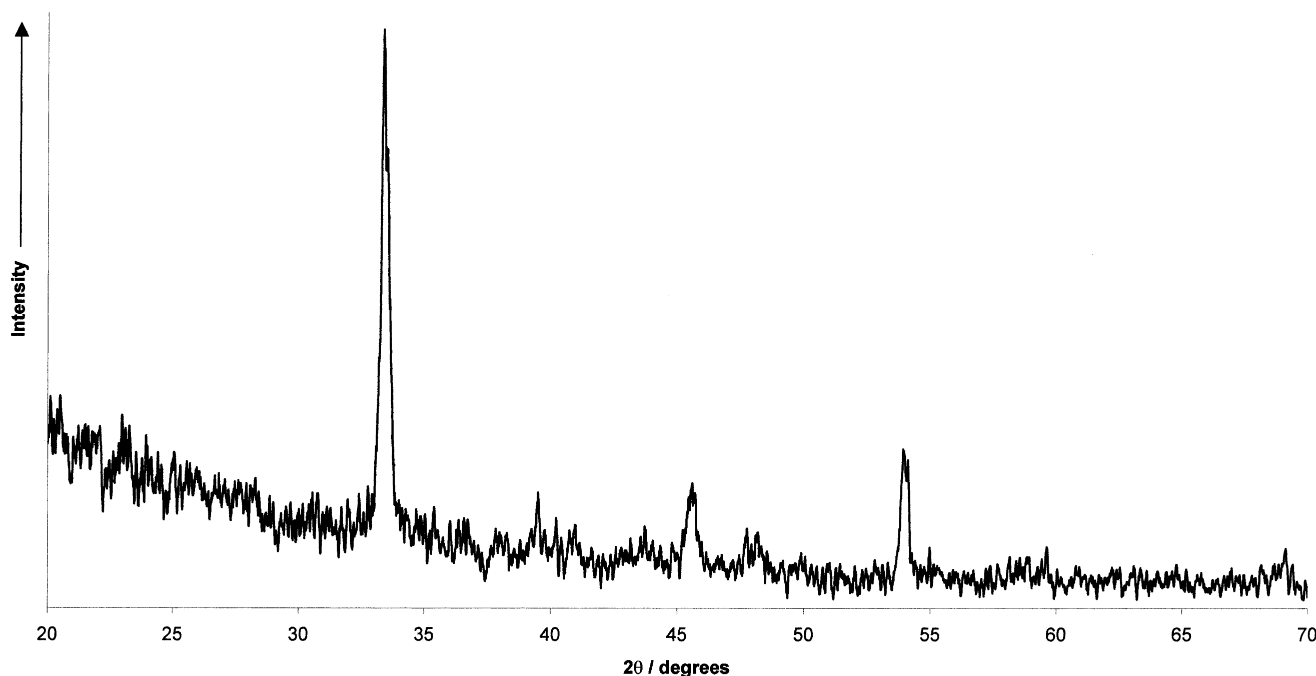


Fig. 2. X-ray powder diffraction pattern of the TiS_3 film formed on glass from the APCVD of $TiCl_4$ and $(CH_3)_3C–S–S–C(CH_3)_3$ at 400 °C.

structure is more open and the TiS_2 particles are typically 300 nm in length. At 450–600 °C, an open mosaic-type morphology is seen of inter-grown needles (Fig. 5). The plates become more defined and somewhat longer and thinner at the highest deposition temperatures. Notably the appearance of the needle features corresponds with the onset of crystallinity as seen by XRD.

EDAX revealed that the films contained titanium and sulfur. The majority of the films showed a Ti:S ratio close to the expected TiS_2. However, films formed from reaction of $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$ and $TiCl_4$ at 250–

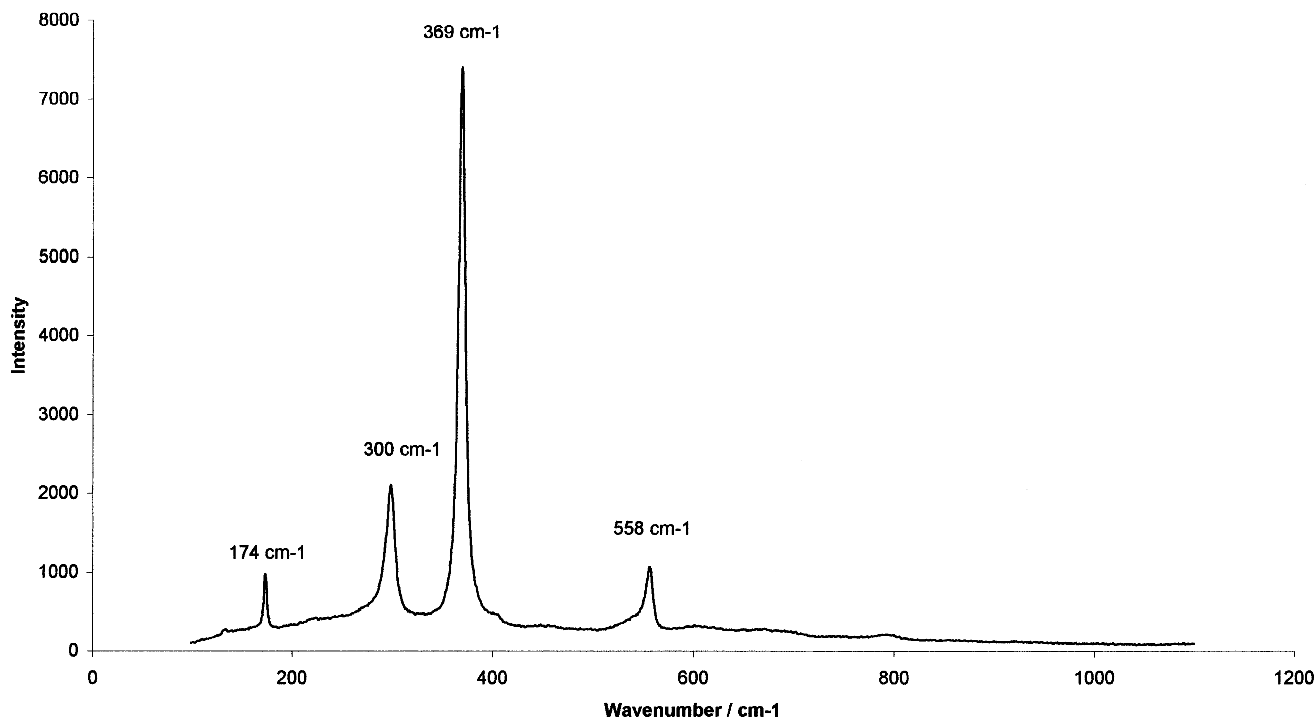


Fig. 3. Raman pattern obtained for the film formed on glass from the APCVD of $TiCl_4$ and $(CH_3)_3C{-}S{-}S{-}C(CH_3)_3$ at 350 °C.

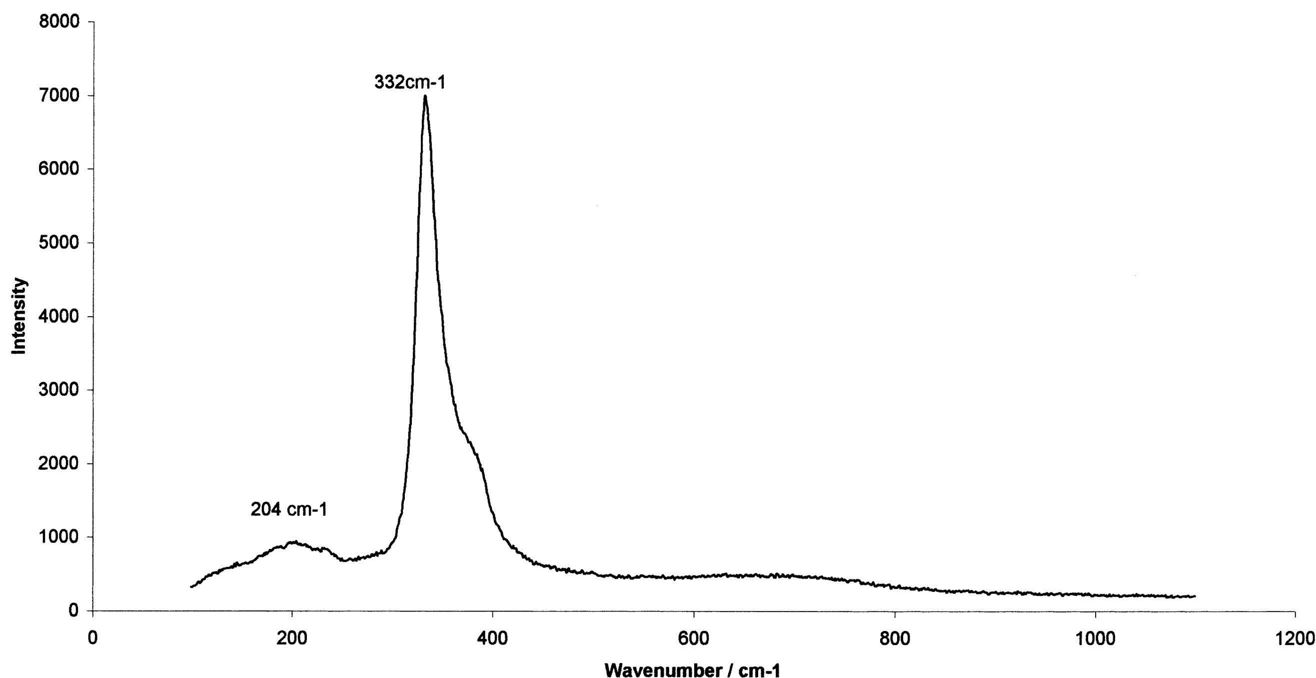
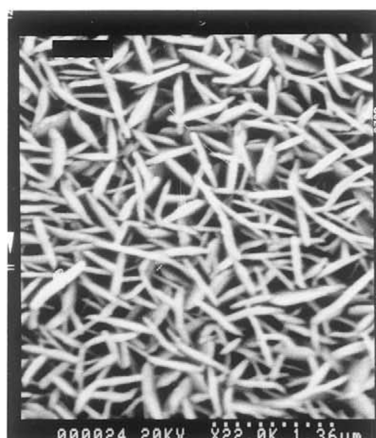


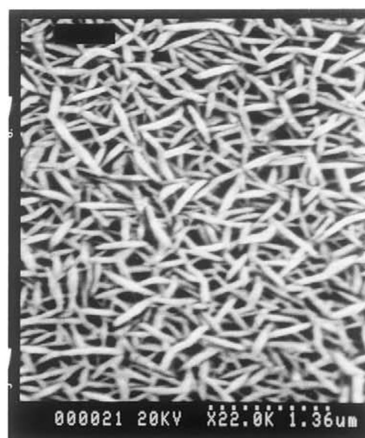
Fig. 4. Raman pattern obtained for the film formed on glass from the APCVD of $TiCl_4$ and $S(Si(CH_3)_3)_2$ at 550 °C.

400 °C showed significantly higher sulfur contents best described as TiS_3. Notably no chlorine or carbon was noted in the films by EDAX. Some breakthrough to the underlying glass was noted during the EDAX analysis, this hampered detection of any oxygen impurities in the films.

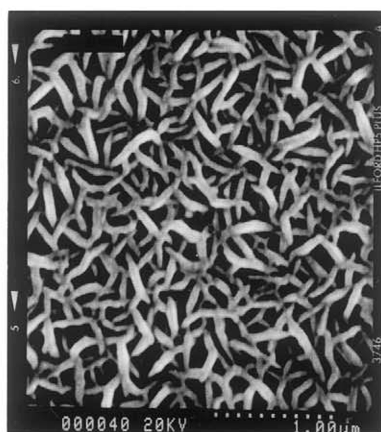
Film contact angle measurements for water droplets showed that the films were hydrophobic with values in the range 80°–100°. This was significantly higher than the plain glass used as a substrate for the depositions that gave values from 40° to 50°. The films were analysed to see if they showed any photocatalytic



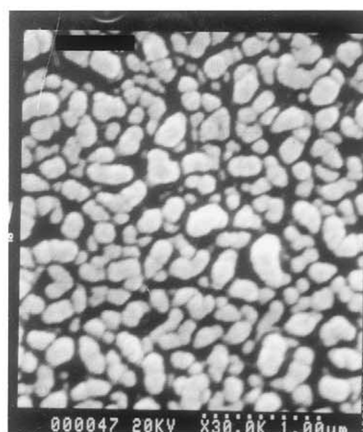
550 °C



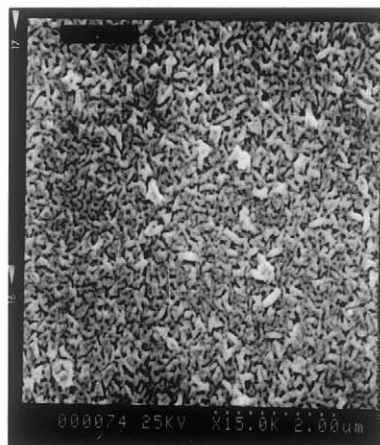
500 °C



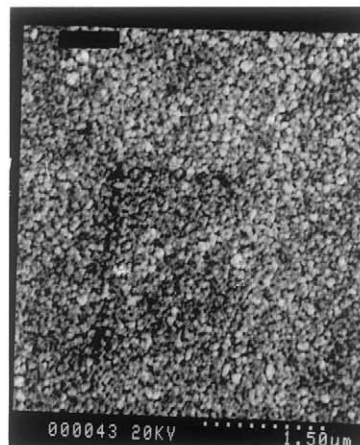
450 °C



400 °C



375 °C



325 °C

Fig. 5. Scanning electron micrographs of the films produced form the APCVD of $TiCl_4$ and $HSC(CH_2)_2SH$ at 325–550 °C.

activity for the destruction of a test organic chemical stearic acid. TiS_2 was ineffective in the destruction of stearic acid upon illumination with 254 nm radiation and showed the same negligible degree of photoactivity as plain glass. Although the stearic acid test may seem a bit esoteric, it indicates that the films are almost certainly not contaminated with TiO_2 as this is a very effective photocatalyst for the destruction of stearic acid even at low concentrations.

A number of different sulfur sources were reacted with $TiCl_4$ under APCVD conditions. There was surprisingly little difference in the chemistry. All the precursors formed single-phase TiS_2. The film growth was extremely fast and mass transport limited showing very little variation in growth rate with temperature at 250–400 °C. Depositions could be initiated at substrate temperatures of 230–275 °C for all precursors. The only deviation from the formation of TiS_2 films was for the reaction of $TiCl_4$ and $(CH_3)_3C–S–S–C(CH_3)_3$ at substrate temperatures of 400 °C and below. The presence of this phase indicates that $(CH_3)_3C–S–S–C(CH_3)_3$ undergoes a different reaction pathway to the other precursors, most probably by keeping the disulfide unit in tact and hence giving a more sulfur-rich source and encouraging the formation of TiS_3. At substrate temperatures above 400 °C, TiS_3 is thermodynamically unstable with respect to sulfur loss and hence the TiS_2 phase is formed.

Previous work has shown that low-pressure chemical vapour deposition (LPCVD) of $TiCl_4$ and $(CH_3)_3C–S–S–C(CH_3)_3$ (1.5 Torr) formed mixed phases of TiS_2 and TiS_3 at deposition temperatures of 300–350 °C and single-phase TiS_2 above 400 °C. The film morphology and properties from this study were somewhat similar to the atmospheric pressure CVD presented here. Notably the growth rates of the APCVD derived films were somewhat faster [19]. Previous work on the LPCVD TiS_2 on glass required the surface to be pretreated with thiol prior to deposition to avoid significant contamination of the product with titanium dioxide [20]. The production of a secondary oxide phase was not found to be a problem in the APCVD process reported here. Further, previous work with $TiCl_4$ and H_2S produced powdery non-adhesive films of TiS_2. This is probably a consequence of rapid gas-phase nucleation effectively “snowing” TiS_2 onto the surface. This was not found to be a problem in the APCVD reactions from any of the sulfur precursors tested in this study.

4. Conclusion

Dual source CVD reaction of $TiCl_4$ and a range of sulfur precursors $S(Si(CH_3)_3)_2$, $HS(CH_2)_2SH$, $HSC(CH_3)_3$ and $S(C(CH_3)_3)_2$ produce films of TiS_2 or TiS_3 on glass substrates. The films were adherent, highly reflective with an attractive gold colouration. They showed good chemical composition and were not contaminated to detection limits with chlorine or oxygen. TiS_2 films showed good electrical conductivity consistent with a semi-metal.

Acknowledgements

The EPSRC is thanked for a grant to I.P.P. for purchase of the Raman microscope and for providing a studentship for E.S.P.

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