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The dual source APCVD of titanium nitride thin films from reaction of hexamethyldisilazane and titanium tetrachloride

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Atmospheric pressure chemical vapour deposition reaction of $TiCl_4$ and $NH(SiMe_3)_2$ at 300–550 °C produced films of titanium nitride on glass substrates. The films were gold or purple/gold in colour, highly reflective in the infrared but with significant transmittance in the visible. Growth rates were typically 300 nm min^{-1} at 550 °C. The films were uniform, adhesive, abrasive resistant, conformal and hard, being resistant to scratching with a steel scalpel. They also showed no change in optical properties on immersion in common solvents or dilute acids or alkalis (2 M). X-Ray diffraction showed preferred growth in the (2 0 0) direction, typical cell constants of 4.23(1) Å and a crystallite size of *ca.* 200 Å. Raman spectra matched powder samples. SEM indicated the films were composed of *ca.* 200 nm particles. EDAX and electron probe studies showed no carbon or silicon impurities and a titanium to nitrogen ratio corresponding to $TiN_{0.95}$. X-Ray photoelectron spectroscopy gave binding energy shifts for $Ti_{2p3/2}$ and N_{1s} at 455.8 and 396.9 eV respectively. The sheet resistance of the films showed increase conductivity with deposition temperature. The titanium nitride films showed potential for heat mirror applications.

Introduction

Films of titanium nitride have attracted a great deal of attention due to their useful characteristics.[1] They are very resistant to chemical attack, refractory and have high hardness that makes them invaluable in wear-resistant and protective applications.[2] Titanium nitride has a NaCl type cubic crystal structure (*Fm*3*m*), with a bulk lattice parameter of 4.241 Å ($TiN_{1.0}$).[3] It is an interstitial material with nitrogen atoms occupying the vacancies within a close packed metal lattice. The material is non-stoichiometric and can be obtained with composition from $TiN_{0.42}$ to $TiN_{1.2}$, all with the NaCl structure type. The electrical resistivity of bulk $TiN_{1.0}$ at 21.7 $\mu\Omega\ cm^{-1}$ makes it a better conductor of electricity than titanium metal.[4] Titanium nitride films have been used as both electrically conducting and barrier layers in microelectronic devices.[5,6] They have found extensive usage for the coating of tool bits and machine parts, for example, in the colour coding of parts for jet engines. Highly pure titanium nitride films are reflective and have a gold hue that has been used in jewellery and in optical applications.[7] It is often difficult to generate gold coloured TiN films because of incorporation of other elements in the films, notably carbon and oxygen that can give the films a brown, black or grey colouring. Some films have been classified as TiN with over 40 atom% carbon and oxygen contents.[8]

There has been much recent interest in the chemical vapour deposition (CVD) of titanium nitride thin films. Notably from Atmospheric Pressure CVD (APCVD) using titanium amides, $Ti(NR_2)_4$ where $R = Me$, Et, with and without the presence of ammonia as an additional nitrogen source and carrier gas.[9] Other methods have involved the dual source APCVD of TiN from the reaction of $TiCl_4$ and ammonia precursors in the gas phase, however these films often have chloride contamination that makes them unsuitable for microelectronic applications.[10] A further problem of the reactions of $TiCl_4$ with ammonia is the extensive pre-reaction prior to entering the coater. This leads to blockages, gas-phase nucleation, formation of multiple pin-hole defects and non-uniform film coverage.[11]

It has been reported that bulk $Me_3SiNTiCl_3$ can be thermally decomposed to form TiN. This reaction is particularly facile as Me_3SiCl is a good volatile leaving group.[12,13] Following this report we have investigated the bulk reaction of $TiCl_4$ with hexamethyldisilazane (HMDS) as a precursor to bulk TiN. The reaction between Group IV chlorides and HMDS is known and the products have been reported to decompose into nitrides. The reaction between $ZrCl_4$ and HMDS yields an adduct, $[Me_3Si)_2NH{\cdot}ZrCl_4]$, which decomposes to amorphous zirconium nitride evolving Me_3SiCl and HCl.[14] Titanium nitride has also been reported from the bulk decomposition of $Me_3SiHNTiCl_3$.[15]

In this paper we report the APCVD of TiN using $TiCl_4$ and HMDS over a range of deposition temperatures and conditions.

Experimental

Titanium(IV) chloride and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were purchased from Aldrich Chemical Company and used without further purification. Both precursors were loaded into bubblers. Standard float glass with a silica coating was used for the following deposition studies. The glass was cleaned thoroughly prior to use with water followed by propan-2-ol then dried at room temperature in a vertical position. Nitrogen (99.9% BOC) was used as the carrier gas after being passed through an oxygen removal column (CuH). A schematic for the pipe assembly is given in Fig. 1. Further details of the pipe assembly, bubblers and experimental set-up have been previously published.[16] For this series of deposition experiments three independently controlled gas streams ($TiCl_4$, HMDS and nitrogen) are passed into a mixing chamber prior to passing into the reaction chamber. The reactor is a cold wall design similar to those reported by us previously.[17] The substrate is heated on a graphite block that contains a single Whatman cartridge heater. The glass is coated in a horizontal position and has dimensions of 15 cm × 4 cm × 0.3 cm. The temperature of the glass substrate was recorded using an independent thermocouple and compared to the setting of the controlling thermocouple. It was found that there was a temperature variation across the surface of the glass substrate

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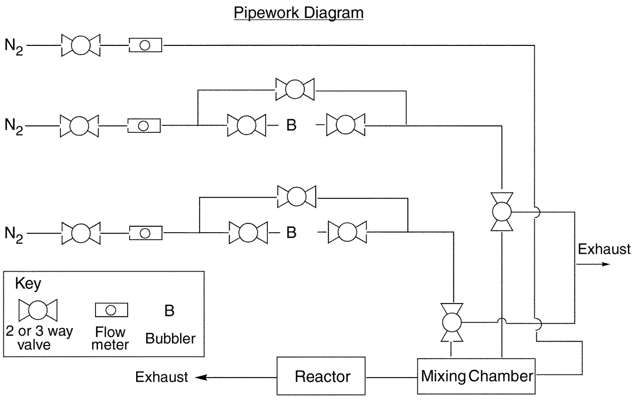

Fig. 1 Schematic of pipe assembly.

of *ca.* 40 °C. All temperatures recorded for the depositions in this report are those of the hottest central part of the glass substrate. Coating temperatures ranged from 300 to 550 °C. All coatings were carried out at atmospheric pressure for 2 minutes. A range of flow rates for all three gas-lines was used.

Glancing angle X-ray diffraction analysis of the films was obtained using a Siemens D5000 diffractometer in the reflection mode (1.5° incidence) using Cu K_α 1.5406 Å radiation. SEM/EDAX was determined on a Hitachi SEM S-570. Electron probe analyses were conducted on a Jeol EMA using polished samples and compared to standards. XPS was performed with a VG ESCALAB 220i XL using focused (300 μm spot) monochromatic Al K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 100 meV. A flood gun was used to control charging and the binding energies were referenced to an advantageous C 1s peak at 284.6 eV. Depth profiles were obtained by using an argon sputtering gun. Reflectance and transmission spectra were recorded between 300 and 2600 nm by an Hitachi U4000 spectrophotometer and between 300 and 1150 nm by a Zeiss miniature grating spectrometer. Raman spectra were obtained on a Renishaw 1000 spectrometer using a Ne excitation laser line. Contact angle measurements were determined by measuring the spread of a 1 μl droplet of water.

Results

Reactions of titanium(IV) chloride with hexamethyldisilylamine (HMDS) under APCVD conditions at 300–550 °C yielded coatings of titanium nitride on SiO_2 coated standard float glass.

The films were analysed using glancing angle XRD, sheet resistance, SEM, EDAX, electron microprobe, contact angle, Raman and UV/vis reflectance and transmission measurements, selected data are given in Table 1. Film quality has been primarily correlated to deposition temperature and resistivity measurements.

The majority of films produced in this series of experiments were gold of uniform thickness across the substrate and free of pin-hole defects. Typical growth rates were 300 nm min^{-1} at 550 °C. Higher deposition temperatures encouraged formation of thicker films. The thickest films were highly reflective and virtually a perfect mirror. These thick films had a gold colour with a slight purple hue in direct reflected light. All films produced by this method were well adhered to the glass substrate and were not removed by placing sticking tape over the film. The films could not be removed by rubbing with a tissue, soft cloth, brass stylus or steel scalpel, indicating that they were extremely hard and typical of TiN films.[5] The TiN films were also unaffected by immersion for 48 hours in water, propan-2-ol, acetone, petroleum spirit, dilute (2 M) mineral acids and alkalis. Contact angle measurements for a water droplet gave values of 80–105°, indicating that the films were hydrophobic. Plain uncoated glass used in this study had a contact angle of 75°.

Flow rates of the precursor and plain nitrogen lines were varied. At higher flow rates (1.5 L min^{-1}) the films covered the whole substrate. At very high flow rates (totalling over 3 L min^{-1}) the deposition became less uniform. For optimisation and coverage of all of the substrate in this particular APCVD set-up, flow rates of 1 L min^{-1} for the plain nitrogen line and 0.3 L min^{-1} for the HMDS and 0.1 L min^{-1} for the $TiCl_4$ line were used.

The films produced in this study are highly reflective and have some transmission in the visible region of the electromagnetic spectrum. Spectra were measured over the region 300–1100 nm on a Zeiss spectrometer for all films and from 300–2400 nm on a Hitachi instrument for selected films. Samples deposited above 500 °C gave good reflection in the near infrared (850–2600 nm) with little reflectance in the visible. Films deposited at higher temperature had greater reflectance in the near IR and less in the visible, Fig. 2. Films deposited at temperatures below 500 °C also had a second reflection maximum centred approximately at 480 nm, Fig. 3. The plain glass used in this study had *ca.* 80% transmission and 10% reflectivity from 400–1100 nm.

Transmission spectra produced from analysing the TiN films showed a correlation with the reflectance spectra, especially those films deposited at higher temperatures where the films transmit visible light and reflect near IR, Fig. 2. The peak transmission was around 550 nm for all samples. The films

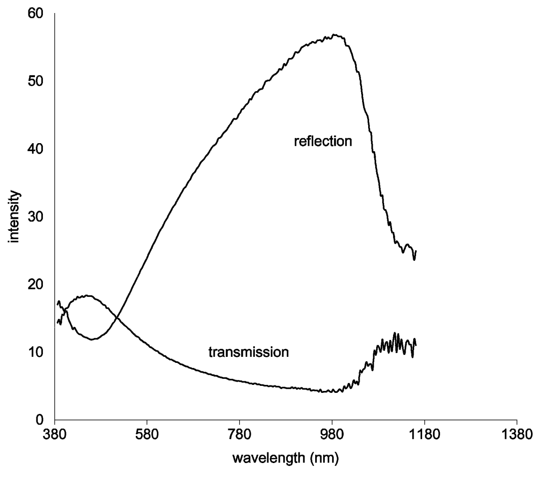

Fig. 2 Reflectance and transmission spectra of film deposited at 550 °C.

Table 1 Experimental conditions and surface analysis results

Deposition temperature/°C	N_2 flow rate through $TiCl_4$ bubbler/L min^{-1}	N_2 flow rate through HMDS bubbler/L min^{-1}	N_2 flow rate/ L min^{-1}	Composition analysis[a]	Lattice parameter *a*/Å
350	0.25	0.60	1.0	$TiN_{1.00}$	Amorphous
400	0.25	0.60	1.0	$TiN_{0.85}$	4.22(1)
450	0.25	0.60	1.0	$TiN_{0.80}$	4.23(1)
500	0.25	0.60	1.0	$TiN_{0.95}$	4.23(1)
500	0.25	0.60	2.0	$TiN_{0.95}$	4.23(1)

[a] Composition determined by electron probe and XPS measurements.

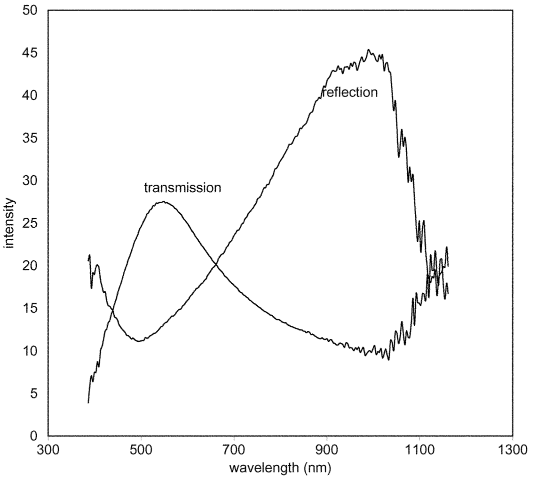

Fig. 3 Reflectance and transmission spectra of film deposited at 350 °C.

deposited at lower temperatures (below 500 °C) have similar spectra to those of the higher temperature samples with a strong transmission in the visible however they also have some absorption in the near IR, Fig. 3.

Scanning electron microscopy of the samples showed particulate films with predominantly uniform shapes with an average particle size of less than 250 nm, Fig. 4.

Sheet resistance of the TiN films was lowered with an increase in deposition temperature. The films deposited at the lowest temperatures had very high resistivities that could not be determined with the current equipment. This change in resistivity has been observed before in APCVD prepared VN and VON films,[16] it can be directly correlated with an increase in crystallite size in the films with increasing substrate temperature. Fig. 5 shows the correlation between deposition temperature and sheet resistance.

Glancing angle XRD of the films showed a single phase of TiN. The peaks are wide with crystallite sizes of the order of 200 Å based on line broadening studies.[17] The (2 0 0) peak was the most intense in all of the spectra, indicating a degree of preferred orientation. Cell parameters of $a = 4.23(1)$ Å were observed. No significant change in cell parameter or crystallite size was noted with deposition temperature.

Electron probe analysis showed a uniform composition across the deposited area. Measurements were taken at 2 mm intervals across the width and length of the sample. These showed a variation in the Ti to N ratio of less than 2 atom%, indicating that the film was extremely uniform in composition. In the majority of samples a composition of $TiN_{0.95}$ was recorded although lower temperatures gave a slightly lower amount of nitrogen. No chlorine was detected by the analysis. Oxygen and silicon were omitted from the analysis as they were already present in the substrate. These results were backed up by EDAX analysis that confirmed the presence of Ti and N and the absence of Cl.

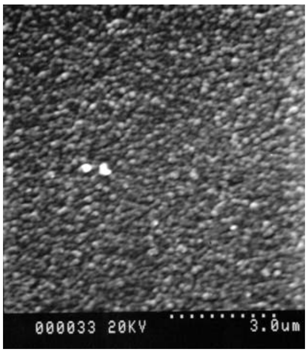

Fig. 4 SEM micrograph of the film produced by APCVD of $TiCl_4$ and HMDS at 450 °C.

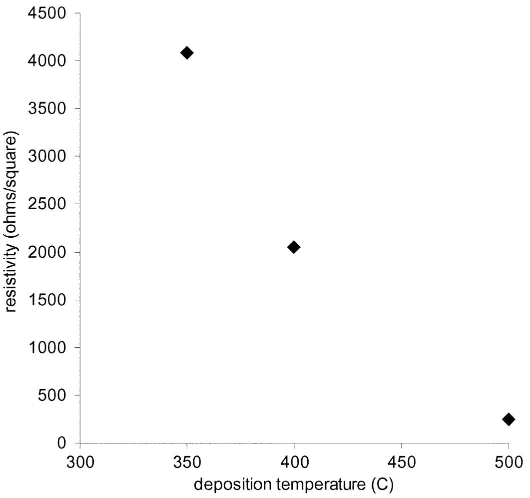

Fig. 5 Sheet resistance *vs.* temperature of deposition.

X-Ray photoelectron spectra of three films were analysed in detail. These showed the presence of titanium, nitrogen and some oxygen in the bulk film. The surfaces of the films were contaminated with some carbon and titania. These were removed to trace levels on subsequent etchings. Bulk Ti_{2p} and N_{1s} XPS binding energies of 455.8 and 396.9 eV matched previous measurements for TiN.[18] The XPS analysis gave a stoichiometry of $TiN_{1.00}$, $TiN_{0.95}$ and $TiN_{0.86}$ for the three samples (Table 1, entries 1, 2 and 5). Some oxygen present as an oxide (O_{1s}, 532.4 eV) was also seen as a minor impurity.[18]

Several broad bands below 550 cm^{-1} were observed in the Raman spectra of the TiN films, these matched measurements on a bulk TiN standard.

Discussion

Reaction of $TiCl_4$ with hexamethyldisilazane under APCVD conditions produced titanium nitride films with interesting optical characteristics, reflecting in the near infrared and transmitting in the visible. These films have good heat-mirror potential. Heat-mirrors have high transmission in the visible (300 nm to 700 nm) while providing high reflectance in the infrared (beyond 800 nm). These films come close to an ideal heat-mirror having maximum transmission in the visible at 580 nm, very close to the human eye's maximum sensitivity to colour; whilst being highly reflective in the infrared. The crossover in the transmission and reflection plots (Fig. 2, 3) is typical of a good heat-mirror.[17] Commercially, ideal heat-mirrors must have the appearance close to that of untreated glass with maximum visible transmission. The method reported here has the potential for producing quality films for practical applications as they combine novel inexpensive precursors with known technology.

Differences in the reflectance and transmission spectra of the films deposited at various temperatures can be explained by changes in crystallinity. Films deposited at lower temperatures had poorer crystallinity giving rise to a reflectance around 480 nm and weaker reflection in the infrared. This change in crystallinity is also seen in the sheet resistance measurements. Higher deposition temperatures lead to lower sheet resistance.

The electron probe analysis indicated an absence of chlorine and carbon in the films, this was confirmed by XPS. This implies a clean decomposition of the precursors during the APCVD process that contributes to the good optical properties of the films. The electron probe analysis in some of the samples also indicated a slightly lower ratio of Ti : N than expected. XPS showed that the deficit of N is probably made up with oxygen (*ca.* 2–3 atom%). It is probable that this oxygen was present in the nitrogen carrier gas used in these experiments.[16] There is also a possibility there could be oxygen present as titanium oxychloride present in the starting reagent. The presence of the oxygen has little detrimental effect on the optical properties of the films. It should be noted that the amount of oxygen found in these films is below that found by single source methods. It is also significantly below that found in TiN and VN films formed by the APCVD of $TiCl_4$ or VCl_4 and ammonia.[16] In those reactions oxygen concentrations of 20 atom% were common.

In the dual source reactions of ammonia and MCl_4 ($M = Ti$, V) gas phase nucleation was a real problem and extensive pin-hole defects were noted in the films.[16,17] It was further noted that extensive nucleation gave rise to severe blockages in the pipework. In contrast, films formed from the APCVD of HMDS and $TiCl_4$ were free from pin-hole defects and gave uniform coverage of the substrate. Interference fringes due to changes in film thickness were also not apparent. The films had a gold coloration, whereas the comparable $TiCl_4/NH_3$ reaction at similar temperatures gave films which were brown/yellow and less reflective. These facts indicate that gas phase nucleation is less of a problem in the HMDS/$TiCl_4$ APCVD reactions. This is probably because the gas phase reaction between HMDS and $TiCl_4$ is less extensive probably because of the steric size of the $SiMe_3$ groups. Interestingly, despite the presence of silicon and carbon in the HMDS, these elements could not be found in the films. This indicates that elimination of Me_3SiCl is extremely facile, and it is this that provides the driving force for the APCVD reaction. An idealised form for this process is shown in Eqn. (1).

$$TiCl_4 + 2NH(SiMe_3)_2 \rightarrow TiN + 4SiMe_3Cl + N_2 + H_2 \quad (1)$$

SEM analysis shows that these films are made up of uniform particles suggesting a degree of crystallinity. However the XRD data show that although a single phase of TiN is clearly identifiable, the films are not completely crystalline, with average crystallite sizes from line broadening studies on the order of 200 Å. The deposition temperature needs to be elevated or the films need to be annealed at a higher temperature to induce further crystallinity.

Conclusions

Titanium(IV) chloride reacts with hexamethyldisilazane under APCVD conditions, to form uniform gold films that have optical properties suitable for heat-mirror applications. The composition of these particulate films has been confirmed to be $TiN_{0.85-1.00}$. This is an inexpensive method utilising known technology with readily available precursors that yields high quality films. Use of hexamethyldisilazane as a nitrogen source has distinct advantages when compared to ammonia. The films obtained are more uniform and free of pin-hole defects. The CVD process also does not have major problems associated with fast reaction kinetics, such as extensive pre-reaction and blockage of the control lines. Despite use of a silicon-containing precursor no silicon was found incorporated in the product.

Acknowledgement

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