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Substrate Effects on the APCVD Growth of Titanium Nitride Films

S.E. Johnson and J.R. Owen

University of Southampton, Southampton, SO17 1BJ, U.K.

Abstract.
Titanium nitride thin films were deposited by atmospheric chemical vapour deposition in the temperature range 560°C to 660°C from titanium tetrachloride and ammonia in argon carrier gas and studied in terms of nucleation and growth, crystalline orientation and impurities. The films were deposited in a cold wall, atmospheric pressure CVD reactor designed to encourage laminar flow conditions and accommodate a number of different substrates under similar temperature and mass transport conditions. Characterisation of the films using scanning electron and atomic force microscopy showed an increase in nucleation density and decrease in surface roughness with temperature. Glancing-angle X-ray diffraction determined the crystallinity and orientation of the films with respect to the substrate and deposition temperature. Films deposited on Si,N, showed preferred orientation whereas those on glass showed random orientation. Energy dispersive spectroscopy calibrated by Rutherford backscattering spectroscopy indicated that the amount of chlorine and oxygen contamination decreased with increasing temperature. RBS also determined the stoichiometry of the titanium nitride films. Resistivity and optical studies were also carried out on titanium nitride thin films on glass to evaluate their suitability as heat mirrors.

1. INTRODUCTION
Titanium nitride is a gold coloured solid that is almost as hard as diamond (9-10 Mohs [1]), has a greater electrical conductivity than titanium metal ($\sigma_{\text{TIN}}=4608\text{kSm}^{-1}$, $\sigma_{\text{Ti}}=2381\text{kSm}^{-1}$ [1]), and is highly reflective in the infrared region of the electromagnetic spectrum while transmitting in the optical region. These properties have lead to research into uses for machine tool coatings, aluminium diffusion barriers in integrated circuits and heat mirror applications (a thin layer of TiN appearing green in transmission). Heat mirrors are of environmental importance since they reduce space heating in cold climates or air conditioning requirements in equatorial climates thus reducing energy consumption. Titanium nitride is deposited by both physical and chemical vapour deposition techniques. Chemical vapour deposition from titanium tetrachloride and a nitrogen and hydrogen mixture is thermodynamically favourable at 850°C but temperatures above 1000°C and as high as 2000°C [2-5] are generally used for durable machine tool coatings since this produces high quality very hard wearing TiN. However these conditions are too harsh to be applied to integrated circuits and limits coating applications on glass. Physical vapour deposition from Ti targets and nitrogen in argon produces high purity TiN on temperature sensitive substrates, such as those used in IC technology, but unsuitable for large area deposition [6]. TiN from metal organic precursors such as tetrakis-dimethylamide titanium and ammonia brings the deposition temperature by CVD down to approximately 200°C to 300°C but these films suffer carbon, hydrocarbon, carbide and oxygen impurities [7-12]. Other more reactive species are being considered such as titanium azides (Cp,Ti(N$_3$)$_2$) [13] and FTi[N(SiMe$_3$)$_2$]$_3$ [14]. Kurtz and Gordon looked into the atmospheric pressure chemical vapour deposition of titanium nitride from titanium tetrachloride and ammonia (450°C to 750°C) [4] which react at room temperature to form a complex. This then decomposes with further heating to form TiNCl at 350°C and TiN above 450°C as researched in the early 1950s by Fowles and Pollard, Antler and Laubengayer [15,16]. At lower temperatures (450°C to 600°C) the TiN thin films suffer some chlorine and oxygen contamination and growth rates are slow compared to OMCVD routes. The majority of research has been into low pressure CVD of this chemistry [17] so Kurtz and Gordon's paper will be
cited most in this present research. Although this process would be unsuitable for IC technology it could be applied to heat mirror coatings.

2. EXPERIMENTAL

2.1 CVD Reactor

Titanium nitride thin films were deposited in an atmospheric pressure cold wall reactor designed to encourage a laminar flow regime (Figure 1). The rectangular channel containing the substrates was formed from two machined graphite blocks (EY308 carbon) producing a channel 40mm x 5mm (w x h) with a 1mm thick recess in the lower block holding 1mm thick substrates. A heater cartridge was inserted into a precision machined socket in the lower block ensuring good thermal contact. A silica tube held the blocks and contained a baffle disk at the inlet to mix the precursors entering the tube via two separate silica inlet tubes. The glass bubbler, containing approximately 5cm$^3$ TiCl$_4$ liquid, had a purge bypass with flow directions controlled by Youngs taps and connections to the furnace inlet and drying columns, upstream, were by greaseless ball joints.

Ammonia gas (99.98% purity) diluted in argon (99.998% purity) was passed through a drying column containing calcium oxide and molecular sieve. Argon flowing through the bubbler was passed through a drying column containing just molecular sieve. The bubbler, delivery line to the furnace and the deposition region of the furnace were insulated with Kao wool to facilitate temperature control of the furnace and bubbler, and prevent condensation of TiCl$_4$ vapour and TiCl$_4$·xNH$_3$ complex before reaching the deposition region.

2.2 Preparation and Deposition

Silica coated glass (an Na blocker commercially available as 'Permabloc'), low sodium glass (Corning 7059) and silicon nitride (0.08$\mu$m thick) coated single crystal silicon wafers were used as substrates for the deposition of titanium nitride from 560°C to 660°C in increments of 10°C. All substrates were prepared by soaking in propan-2-ol then de-ionised water in an ultrasonic bath and dried at 110°C in an oven. The silicon nitride surface was featureless when observed at 15,000 magnification by scanning electron microscopy. The furnace was purged in a 170cm$^3$/min argon flow while warming to the required deposition temperature. The ammonia was introduced (100cm$^3$/min) at approximately 100°C below the deposition temperature to allow flow stabilisation and to produce a slightly reducing atmosphere in the reactor. Bubbler warm up to 50°C was initiated when the furnace reached 50°C below the deposition temperature. At 50°C the vapour pressure of the TiCl$_4$(l) was 44mmHg. 70cm$^3$/min argon was redirected...
from the purge bypass through the TiCl₄ precursor to initiate deposition. The remaining 100cm³/min argon was used to dilute the ammonia. Depositions were for 40 minutes and the samples were then allowed to cool in a flow of 50cm³/min argon to room temperature.

2.3 Methods of Analysis
All samples were analysed by scanning electron microscopy (SEM), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and glancing-angle X-ray diffraction (GA-XRD). The EDS was calibrated by comparing the Rutherford backscattered data of a titanium nitride thin film deposited on pyrolytic graphite with the EDS data of the same sample. The optical properties and sheet resistance were also investigated.

Average crystal sizes and nucleation densities were determined by observation under SEM (JEOL JSM-6400) and AFM (Topometrix TMX 2010). At deposition temperatures above 600°C the individual crystals were too small to be resolved by SEM and AFM was used. SEM micrographs were taken at a magnification of 10,000, and 75μm and 1μm scanners were used for AFM giving images 5 x 5μm and 1 x 1μm. The film thickness was determined by observation at 45° incidence under a scanning electron microscope at 10,000 magnification. All TiN films on glass substrates had to be vacuum coated with a 20nm gold layer to prevent charge accumulation in the glass when studying at 45°. The gold coating was only applied once all other analyses had been carried out.

3. RESULTS AND DISCUSSION
All films were rose gold in reflection and thinner films were green in transmission. A decrease in surface roughness could be seen by the naked eye as films deposited at lower deposition temperatures (560°C) scattered light, appearing slightly blue on the surface, indicating a surface roughness of at least 380nm. Films deposited at higher deposition temperatures were highly reflective and appeared to be optically flat. All films on glass were gold and highly reflective when observed from beneath, through the glass substrate. X-ray diffraction of dark blue crystalline powder deposited at the furnace inlet proved that TiNCl was being formed upstream of the deposition area.

3.1 Crystal orientation
Glancing-angle X-ray diffraction was carried out on samples deposited at 570°C, 600°C, 630°C and 660°C on all substrates. Titanium nitride on low sodium glass and silica coated glass showed a polycrystalline Osbornite structure with random orientation with a slight preference towards (200) whereas titanium nitride on silicon nitride showed the polycrystalline structure but with a definite (200) preferred orientation that became more distinct with increasing deposition temperature. A strong (400) peak from the silicon and a very small shoulder at approx 2θ = 70, due to the thin layer of Si₃N₄, can also be seen from the substrate. See figures 2 and 3.

Figure 2: Titanium nitride on silicon nitride
Figure 3: Titanium nitride on low sodium glass
3.2 Nucleation and Growth

Nucleation and growth of titanium nitride on different substrates was scrutinised by studying the nucleation densities and average crystal size of each sample with respect to the surface chemistry of the substrate and the deposition temperature. In general crystals on silicon nitride were more well defined as octahedra with clean facets compared to those on silica coated glass and low sodium glass which were more nodular. Figure 4 shows the columnar growth exhibited by all titanium nitride deposits on all substrates. In the case of columnar growth the lateral crystal size, ie the width of the columnar crystal, was determined by the density of nucleation at the initial stage of film growth. The crystal size, viewed from above the film, varied with position on the substrate (figures 5 and 6). Crystals upstream were smaller than those downstream of the precursor flow. The density of nucleation can be related to the conditions present at the start of growth. Normal crystallization requires surface diffusion to transport molecular products as fast as they are formed from the initial point of deposition to a growing nucleus at another point on the surface. In cases where fast kinetics produce material at a higher rate than that of diffusional transport the molecular concentration can rise to a point where new nucleation occurs.

The situation leads to a high density of nuclei forming before the surface is completely covered. However, homogenous nucleation in the gas phase must also be considered as a contributing factor towards the larger nucleation density upstream. The gaseous precursor concentration will be highest at the furnace inlet leading to a much greater probability of homogenous nucleation upstream than downstream where the concentrations are much depleted. These gas phase nuclei may then settle on the substrate and form new growth centres. Another consideration must be the presence of more corrosive by-products (eg HCl) downstream that may etch new nuclei.

The lateral crystal size of titanium nitride films on silica coated glass, and silicon nitride were studied with reference to the deposition temperature by observation with atomic force microscopy. The number of crystals per square micron was determined, then the average crystal size calculated for each sample. The effects of temperature increase are two fold: first we may expect the reaction kinetics to increase with temperature; second, the surface mobility of the products can also increase. The result indicates that the effect of temperature is greatest on the latter at temperatures up to 850K. Above this we observe a decrease in crystal size. This is most probably due to the reaction rate becoming more temperature sensitive with nuclei forming faster than the product is able to diffuse across the surface to an already established growth centre.
As can be seen from figure 7, TiN on silica coated glass and low sodium glass follow similar trends: an almost steady value at lower temperatures followed by a sudden increase to the maximum size (0.118μm² at 883K on the silica coating, 0.018μm² at 903K on 7059 glass). The crystal size then decreases just as suddenly. TiN on silicon nitride also shows an increase and decrease but the variation is less severe and the increase is immediate. TiN on silica coated glass produced the largest crystals with those on low sodium glass and silicon nitride producing crystals of a similar size. The increase and decrease in lateral crystal size was accompanied by an increase in film thickness which then levelled at the higher temperatures (figure 8).

### 3.3 Impurities

EDS was used to determine the ratio of chlorine contamination to titanium content calibrated by RBS. The ratio was calculated by measuring the Ti and Cl peak heights of each sample. It can be seen from figure 9 that the chlorine content decreased with increasing deposition temperature as expected [4]. The lowest chlorine contamination values were for TiN deposits on silicon nitride. This was as expected since no sodium would be present in these substrates. Figure 10 shows an unusual feature of concentric ring patterns incorporated in amongst the TiN crystals. EDS analysis of areas of high concentration of these crystals showed a large amount of sodium and chlorine contamination. This sodium chloride was probably formed by the reaction: 2Na₂O + TiCl₄ → TiO₂ + 4NaCl.
The symmetry of the rings (30µm spacings) suggests that Na' emanated from point sources at the centres ie that the contamination was due to pinholes in the SiO₂ coating rather than a uniform diffusion through the layer with each ring being a super-saturation point. The rate of surface diffusion of Na' was calculated to be approximately 0.01µm/s. The oxygen contamination was minimal, approximately 2-5 at% with the Cl:Ti ratio varying from 0.15 to 0.03 at for TiN on Si₃N₄ and 0.12 to 0.04 for TiN on low sodium glass. RBS revealed that the titanium nitride film on pyrolytic graphite deposited at 630°C (down stream of all other substrates) was slightly substoichiometric: Ti = 53.6 at%, N = 42 at%, (O ≤ 1.7 at%, Cl ≤ 2.6 at%). It was noticed that the ratio of Cl:Ti decreased with age of the sample. This may be due to outgassing of chlorine from grain boundaries.

3.4 Resistivity
Sheet resistance measurements (ρₛ) were made with a four point probe using a current of 1mA. With knowledge of the film thickness these measurements could be used to calculate the specific resistance (ρₛ). Titanium nitride films on silica coated glass had specific resistance values of 250µΩ-cm to 4760µΩ-cm which are comparable to those quoted by Kurtz and Gordon [4] of 200µΩ-cm to 6000µΩ-cm. Specific resistance values of TiN on Si₃N₄ were generally less, 150µΩ-cm to 1500µΩ-cm (figure 11). The sheet resistance decreased with increasing deposition temperature in accordance with the decrease in chlorine contamination for titanium nitride thin films deposited on silicon nitride and silica coated glass (figure 12).

3.5 UV to NIR spectroscopy
The requirements for heat mirror coatings are a medium to high transmittance in the visible region and high reflectance throughout the infrared region to reduce heat transfer across the coated window [18]. The reflectance and transmittance of titanium nitride thin films on silica coated glass and low sodium glass was measured from 0.3µm to 2.5µm. Figures 13 and 14 show the reflectivity minimum moving towards shorter wavelengths at increasing deposition temperatures. Reflectivity minimums varied from λₘᵦᵳ₉ = 505nm (Tₘᵢ₉ = 640°C and 630°C on low sodium glass) to λₘᵦᵳ₉ = 580nm (Tₘᵢ₉ = 560°C on silica coated glass). This compares with approximately 590nm to 650nm in Kurtz and Gordon's paper [4], calculated from figure 4a (p284). The slope of the point at which the reflectivity increases became steeper with increasing deposition temperature. Although the reflectivity in the NIR region (1.0 µm to 2.5 µm) generally increased with increasing deposition temperature, the maximum reflectivity with the most uniform reflectance across the NIR region was found to be for a deposition temperature of 600°C on silica coated glass and 580°C on low sodium glass.
4.0 Conclusion

Titanium nitride thin films deposited by AP-CVD from titanium tetrachloride and ammonia in argon were polycrystalline in structure with a slight preference in orientation towards $(200)$ when deposited on silica coated glass and low sodium glass. TiN on silicon nitride showed a clear preference towards $(200)$ which became more defined at higher temperatures. The lateral crystal size depended upon both deposition temperature and position with respect to the precursor flow. An increase and decrease in crystal size with deposition temperature on all substrates indicated an increase in surface diffusion with temperature for the lower temperatures and a change to faster reaction kinetics over the higher temperatures. The larger crystal size downstream of the precursor flow was due to a depletion in precursor concentrations above the substrate surface leading to a lower nucleation density. Chlorine concentration in all films decreased with increasing deposition temperature as expected. The sheet resistance of TiN on silica coated glass and silicon nitride also decreased with increasing temperature but more strongly than the decrease in chlorine. TiN on low sodium glass appeared to be more dependent upon the crystal size than the chlorine content. The best condition for deposition of TiN heat mirror coatings was a deposition temperature of $600^\circ$C on silica coated glass and $580^\circ$C on low sodium glass.

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