Chem. Mater. **1999,** *11,* 3490−3496

Atmospheric Pressure Chemical Vapor Deposition of Titanium Aluminum Nitride Films

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Received March 16, 1999. Revised Manuscript Received October 6, 1999

The atmospheric pressure chemical vapor deposition of titanium aluminum nitride films was accomplished using a three-precursor system comprised of titanium tetrachloride, *tert*-butylamine, and trimethylaluminum at a substrate temperature of 600 °C. Smooth, specular, and highly adherent violet-black films were obtained. The aluminum content of the films varied with trimethylaluminum flow rate up to a maximum aluminum/titanium ratio of about 1:1. Higher aluminum flow rates afforded rough, poorly adherent coatings. Films having the compositions $Ti_{0.83}Al_{0.17}N_{0.89}$, $Ti_{0.69}Al_{0.31}N_{0.85}$, and $Ti_{0.52}Al_{0.48}N_{1.38}$ were analyzed in detail. The films were characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy, Rutherford backscattering spectrometry, scanning electron microscopy, atomic force microscopy, and resistivity measurements. The films were subjected to nanoindentation hardness testing and high-temperature oxidation studies. The $Ti_{1-x}Al_xN$ films were found to be harder and more resistant to oxidation by ambient atmosphere than TiN films deposited from titanium tetrachloride and *tert*-butylamine at 600 °C. The dependence of the film properties on the aluminum content is discussed.

Introduction

Titanium nitride (TiN) has been the subject of considerable attention in recent years due to its wide range of applications. It is used as a wear resistant coating on steel tools[2] and is also used as a decorative gold-colored coating due to the similarity of its optical spectrum to that of gold.[3] In addition, its optical properties make TiN an excellent candidate for solar control coatings on automotive and architectural glass.[4] The microelectronics industry employs TiN as both a contact material[5] and a barrier layer material.[6]

While TiN has an abundance of useful properties, there are some characteristics that adversely affect its performance in certain applications. Polycrystalline TiN films deposited by CVD methods possess highly ordered columnar grain structures that are oriented perpendicular to the surface of the substrate. The boundaries between the crystalline grains provide fast diffusion pathways for interconnect metals (aluminum or copper) to reach the substrate, especially when very thin barrier layers are used.[7] Another drawback is the relative ease with which TiN is oxidized by ambient air at high temperatures (>500 °C). Certain properties of TiN can be improved by the inclusion of varying amounts of a third element in the film. For example, amorphous titanium silicon nitride films have been reported to have improved barrier layer performance over TiN.[7,8] Titanium boron nitride, titanium carbon nitride, and titanium niobium nitride all have phases that are harder than TiN itself.[9]

Titanium aluminum nitride ($Ti_{1-x}Al_xN$) is the best studied of the ternary titanium nitride materials. It is

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10.1021/cm990157u CCC: $18.00

harder and more resistant to oxidation than TiN.[9−12] Both properties make it a desirable material for application as a wear-resistant coating. The attractive violet-black color of $Ti_{1-x}Al_xN$ has resulted in its use as a durable, decorative coating in jewelry.[11] Low aluminum content $Ti_{1-x}Al_xN$ films have also been shown to be effective barrier layers in microelectronics devices.[13] $Ti_{1-x}Al_xN$ films have been produced by several different physical vapor deposition (PVD) methods.[9,10] A serious problem with PVD approaches is the difficulty of preparing titanium/aluminum targets with specific elemental ratios due to the large difference in the melting points of the two metals. Chemical vapor deposition (CVD) offers improved ability to control the elemental composition of $Ti_{1-x}Al_xN$ films, since the titanium/aluminum ratio should related to the relative flow rates of the respective sources. The only reported CVD routes to $Ti_{1-x}Al_xN$ films have employed the plasma-assisted reaction of titanium tetrachloride and aluminum trichloride with either ammonia or nitrogen gas in the presence of hydrogen or the thermal reaction of tetrakis(methylamido)titanium and hexakis(dimethylamido)dialuminum with ammonia.[12] Plasma-assisted CVD involves expensive equipment relative to thermal CVD, and the use of a plasma can lead to substrate and film damage. Aluminum trichloride possesses a low vapor pressure and its use in a CVD process would require special handling to obtain high growth rates. Moreover, amide-based precursors are more expensive and possess lower vapor pressures than other readily available titanium and aluminum source compounds. For these reasons, we sought to explore chemistry that would lead to a low-cost CVD process for $Ti_{1-x}Al_xN$ films. Herein we report a thermal atmospheric pressure CVD route to $Ti_{1-x}Al_xN$ films. Depositions were conducted using a ternary precursor system consisting of titanium tetrachloride, trimethylaluminum, and *tert*-butylamine. The aluminum/titanium ratio of the films varied with the flow rate of the trimethylaluminum up to a maximum of about 1:1. It was found that the hardness and resistivities of the films increase with increasing aluminum content in $Ti_{1-x}Al_xN$. Finally, $Ti_{1-x}Al_xN$ films produced by our method are substantially more resistant to atmospheric oxidation than TiN itself.

Results

Atmospheric Chemical Vapor Deposition of $Ti_{1-x}Al_xN$ Films. One of us has reported the deposition of TiN films through the atmospheric pressure CVD reaction of titanium tetrachloride and *tert*-butylamine.[14] As shown in Figure 1, we have adapted the reactor employed for TiN depositions to allow fabrication of $Ti_{1-x}Al_xN$ films, using titanium tetrachloride, *tert*-butylamine, and trimethylaluminum as source compounds. An idealized equation for this process is given in eq 1. Each precursor was held in a stainless steel bubbler and was volatilized by passing nitrogen carrier gas through the bubbler at various flow rates. The gaseous precursor streams were fed into an injector that consisted of three concentric steel tubes. The outermost tube delivered the *tert*-butylamine, while the innermost tube supplied the titanium tetrachloride stream. For growth of TiN films, pure nitrogen was passed through the middle tube, while this flow was seeded with trimethylaluminum for $Ti_{1-x}Al_xN$ depositions. Flow rates were first optimized for TiN depositions at a substrate temperature of 600 °C. For subsequent $Ti_{1-x}Al_xN$ film trials, flow through the middle tube was a mixture of a stream of pure nitrogen and a stream containing trimethylaluminum, but the total flow rate from the middle tube was maintained near the optimum value found for pure TiN depositions. $Ti_{1-x}Al_xN$ films were thus deposited on Corning 7059 glass, crystalline silicon, and mica at a substrate temperature of 600 °C using the flow rates described in Table 1. The as-deposited films were highly specular, smooth, adherent (Scotch tape test), and violet-black in color. Films deposited at three different sets of flow rates were analyzed. The bulk composition of films deposited on crystalline silicon was determined by Rutherford backscattering spectrometry (RBS). The results are summarized in Table 1. The intermediate aluminum content film was subjected to forward recoil spectroscopy, which indicated a hydrogen content of ~5−6%. Attempts to deposit films using trimethylaluminum flows of >0.09 mmol/min resulted in blue-black coatings with matte finishes, but these films peeled away from the substrate upon cooling to ambient temperature. Accordingly, our

$$TiCl_4 + t\text{-}BuNH_2 + Al_2(CH_3)_6 \xrightarrow{600\ °C} Ti_{1-x}Al_xN\ \text{films} + \text{volatile byproducts} \quad (1)$$

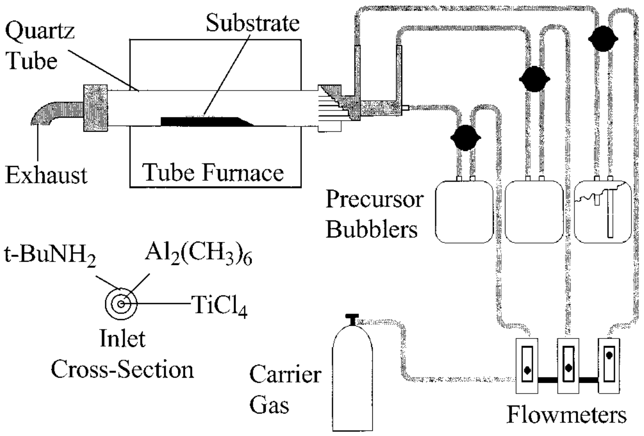

Figure 1. Schematic representation of atmospheric pressure CVD system.

Table 1. Film Composition As Determined by Rutherford Backscattering Spectrometry

flow rates (mmol/min):			
$Al_2(CH_3)_6$	$TiCl_4$	t-$BuNH_2$	film composition
0.02	0.40	4.3	$Ti_{0.83}Al_{0.17}N_{0.89}$
0.06	0.40	4.3	$Ti_{0.69}Al_{0.31}N_{0.85}$
0.09	0.40	5.3	$Ti_{0.52}Al_{0.48}N_{1.38}$

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(11) For a review of ternary nitride films, see: Sproul, W. D. *J. Vac. Sci. Technol. A* **1994**, *12*, 1595.

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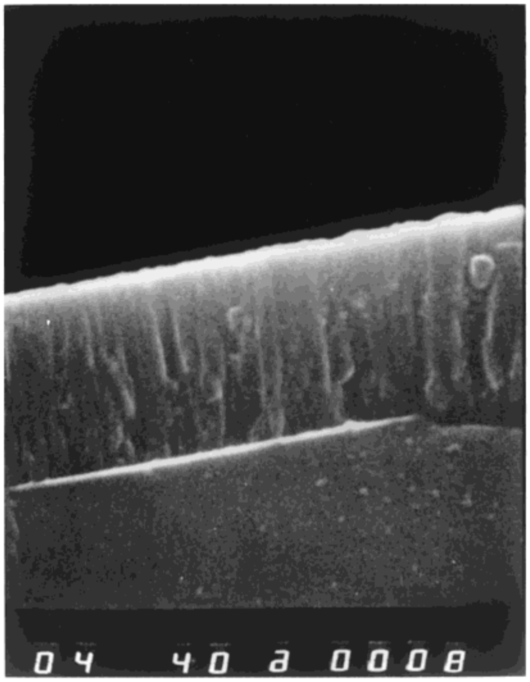

Figure 2. Cross-section electron micrograph of a $Ti_{0.69}Al_{0.31}N_{0.85}$ film grown on Corning 7059 glass at 600 °C. The film thickness is 8000 Å.

process provides high quality, adherent films up to an aluminum/titanium ratio of about 1:1.

The surface composition of a film deposited on Corning 7059 glass was analyzed using X-ray photoelectron spectroscopy (XPS). Prior to analysis, the film was sputtered with argon ions for 1.5 h to remove surface contaminants and amorphous oxides. The XPS spectrum showed the presence of titanium (Ti $2p^{3}/_{2}$ = 455.5 eV, 458.0 eV; ratio = 30:70), aluminum (Al 2p = 74.9 eV), nitrogen (N 1s = 397.1 eV), oxygen (O 1s = 531.5 eV), and carbon (C 1s = 285.0 eV). The two titanium binding energies are close to values that have been previously reported for TiN and TiO_2, respectively.[15] The nitrogen binding energy was also consistent with TiN. The aluminum and oxygen binding energies were consistent with values that have been reported for aluminum oxide (Al_2O_3).[15] After sputtering, the surface was found to have an approximate composition of $Ti_{0.1}Al_{1.0}N_{0.5}O_{1.1}C_{0.1}$. Since the sputtering rate of our instrument is about 0.1 Å/s, this experiment indicates that approximately the first 400−500 Å of the film is oxidized and aluminum rich. Since the RBS data demonstrate that the bulk of the film contains low oxygen levels, the RBS spectrum of a $Ti_{0.69}Al_{0.31}N_{0.85}$ film was reanalyzed to allow modeling of the oxygen content in the surface region of the film. This analysis afforded a composition of $Ti_{0.72}Al_{0.28}N_{0.98}O_{0.22}H_{0.17}$ for the first 300 Å of the film, but a composition of $Ti_{0.72}Al_{0.28}N_{1.09}H_{0.06}$ was modeled for the remainder of the film. Accordingly, the RBS results are consistent with the surface region of the film being oxidized, with the bulk of the film having low oxygen content. The differences between the surface stoichiometries obtained by XPS and RBS might be due to preferential sputtering of titanium during the XPS experiment.

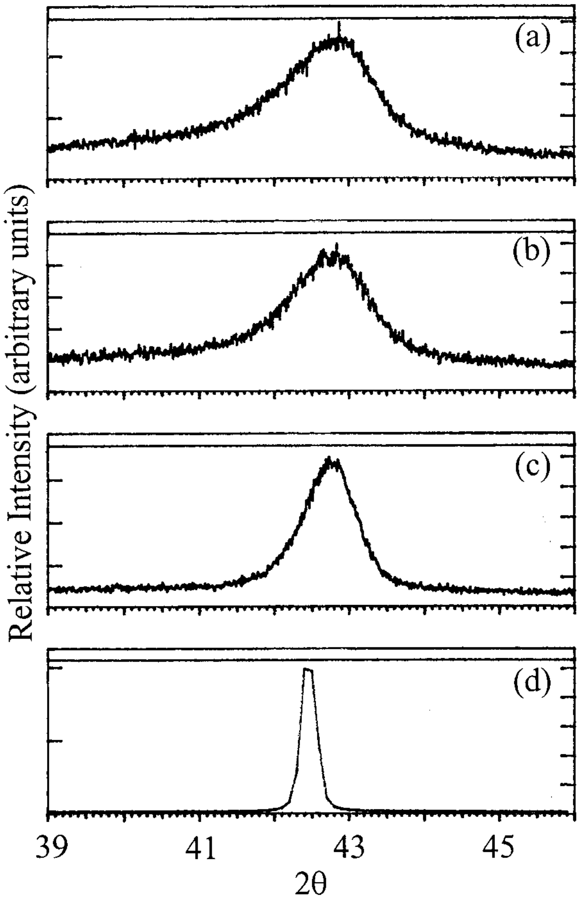

Figure 3. X-ray diffraction spectra of films deposited on Corning 7059 glass: (a) $Ti_{0.52}Al_{0.48}N_{1.38}$, (b) $Ti_{0.69}Al_{0.31}N_{0.85}$, (c) $Ti_{0.83}Al_{0.17}N_{0.89}$, and (d) TiN.

The structure of the films was probed by scanning electron microscopy, atomic force microscopy (AFM), and X-ray diffraction. A cross-section electron micrograph of a $Ti_{0.69}Al_{0.31}N_{0.85}$ film grown on Corning 7059 glass revealed the thickness of the film to be 8000 Å (Figure 2), giving a growth rate of about 0.27 μm/min during a 3-min deposition. The columnar structure characteristic of TiN films was evident in the cross-section micrograph, suggesting that the structure of TiN is conserved upon incorporation of aluminum. X-ray diffraction spectra corroborated this observation (Figure 3). TiN films deposited in this system (trimethylaluminum flow = 0 mmol/min) have an X-ray diffraction pattern consisting of a single reflection corresponding to the (200) orientation at 2θ = 42.5°. X-ray diffraction patterns of the $Ti_{1-x}Al_xN$ films display the same preferred orientation. The absence of any reflections corresponding to aluminum nitride phases suggests that the aluminum was substituted in titanium sites in the TiN lattice, thereby reducing the size of single-crystal domains. Alternatively, AlN was present in amorphous form. A slight increase in the 2θ value of the (200) reflections occurred as the aluminum content in $Ti_{1-x}Al_xN$ increased. The shift is likely the result of a small change in the d spacing of the lattice caused by the difference in size between Al(III) (0.68 Å) and Ti(III) (0.81 Å).[16] Broadening of the (200) reflection with increasing aluminum content was also observed. Generally, broadening of an

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(15) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Murlenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp., Physical Electronics Division: Eden Prairie, Minnesota; 1979; pp 43, 50, 68.

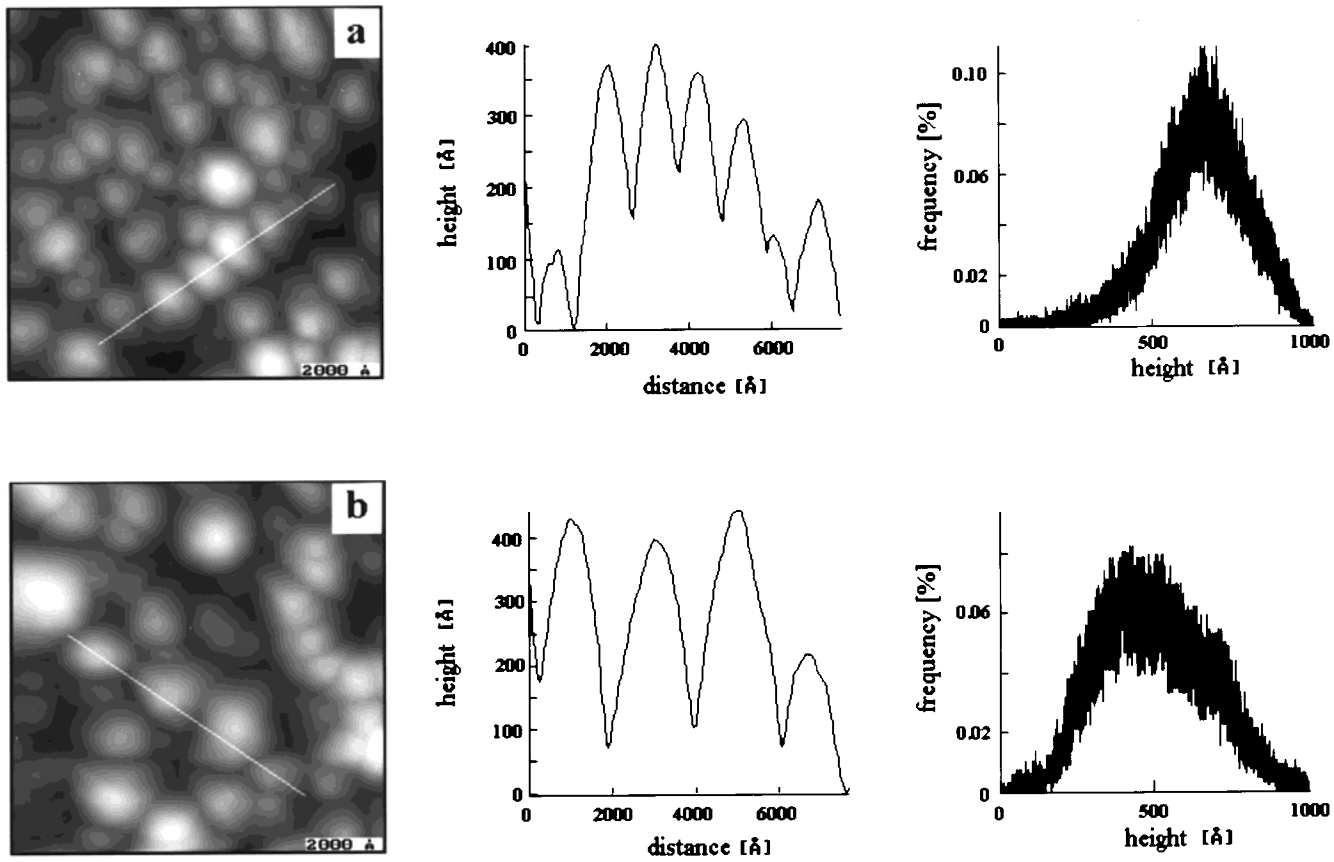

Figure 4. Topographic images of (a) $Ti_{0.69}Al_{0.31}N_{0.85}$ and (b) TiN. The total scan area is 1 × 1 μm^2. The corresponding cursor profiles and histograms are shown in the middle and right columns, respectively.

X-ray diffraction reflection indicates a decrease in the average grain size within the bulk of the material.[17]

The actual shape and size of the crystalline domains at the surfaces were visualized directly using AFM. Figure 4 shows two 1 × 1 μm^2 topographic images for $Ti_{0.69}Al_{0.31}N_{0.85}$ and TiN films, respectively. As shown in the corresponding cursor profiles, the lateral dimension of the $Ti_{0.69}Al_{0.31}N_{0.85}$ crystalline domains ranged from 500 to 1200 Å, with an average size of 750 Å. By contrast, the lateral dimension of TiN ranged from 1200 to 7500 Å, with an average size of 1700 Å. The surfaces of both films have similar roughnesses. The measured z-roughness shown in the histograms in Figure 4 is 400 and 500 Å for $Ti_{0.69}Al_{0.31}N_{0.85}$ and TiN films, respectively.

Incorporation of aluminum altered the physical, electrical, and chemical properties of the film. Properties of the $Ti_{1-x}Al_xN$ films were evaluated and compared to those of TiN (Table 2). The resistivity of the $Ti_{1-x}Al_xN$ films increased by an order of magnitude as x increased from 0 to 0.48. Nanoindentation was used to compare film hardness. The results showed that the addition of aluminum increased the hardness of the films by as much as 13%, compared to TiN (Table 2).

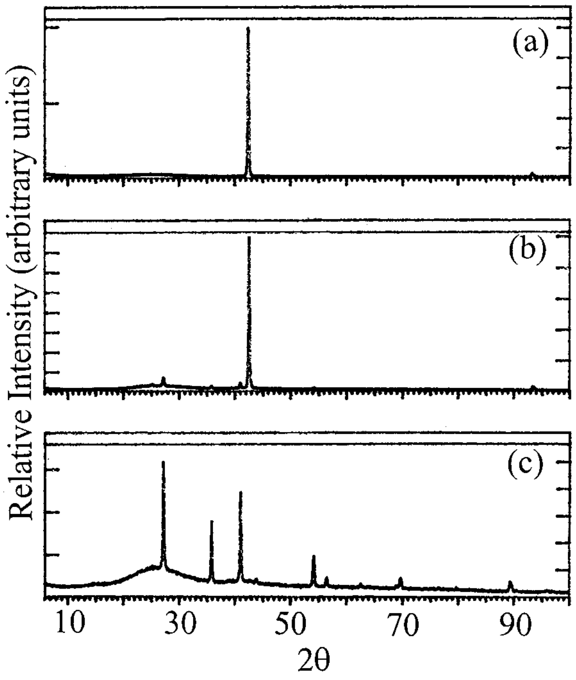

Figure 5. X-ray diffraction spectra of a TiN films deposited on Corning 7059 glass (a) as deposited, (b) after 3 h at 550 °C under ambient atmosphere, and (c) after 3 h at 625 °C under ambient atmosphere.

The resistance of the films to high-temperature oxidation by ambient atmosphere was also evaluated. Films were positioned on a steel stage in a quartz tube open to air at both ends. The tube was placed in a tube furnace and was heated for 3 h at 550, 625, and 700 °C. The films were analyzed by X-ray diffraction before and after heating (Figure 3). The as-deposited TiN film was

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(16) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York; 1988; pp 1387−1388.

(17) Cullity, B. D. *Elements of X-ray Diffraction*; Addison-Wesley: Reading, Massachusetts; 1978; p 281.

Table 2. Properties of TiN Films Deposited on Corning 7059 Glass

composition	resistivity ($\mu\Omega$ cm)	hardness (N/mm^2)
TiN	1 020	11 700
$Ti_{0.83}Al_{0.17}N_{0.89}$	1 440	11 900
$Ti_{0.69}Al_{0.31}N_{0.85}$	7 920	13 000
$Ti_{0.52}Al_{0.48}N_{1.38}$	9 920	13 200

specular and bright gold-colored. After heating at 550 °C for 3 h, the TiN film lost much of its metallic sheen and showed new reflections in the X-ray diffraction spectrum corresponding to TiO_2 (rutile).[18] The (200) TiN reflection was still present but was reduced in intensity. A TiN film was completely oxidized to TiO_2 after 3 h at 625 °C. A $Ti_{0.69}Al_{0.31}N_{0.85}$ film, however, was unchanged after heating for 3 h at 625 °C under ambient atmosphere. After heating for 3 h at 700 °C in air, a $Ti_{0.69}Al_{0.31}N_{0.85}$ film lost some of its luster and the color changed to a bluer tint, but there were no reflections from TiO_2 in the X-ray diffraction spectrum.

Discussion

We have developed a CVD process for $Ti_{1-x}Al_xN$ films by adding a flow of trimethylaluminum to an existing process for TiN films[14] that uses titanium tetrachloride and *tert*-butylamine as the source compounds. Our process affords $Ti_{1-x}Al_xN$ films up to $x = 0.5$; above this stoichiometry, poorly adherent films resulted. Several studies have found that $Ti_{1-x}Al_xN$ films made by reactive sputtering revealed reflections in the X-ray diffraction spectrum due to the cubic TiN phase when $x \leq 0.5$, but with $x = 0.7$ reflections originating from both cubic TiN and wurtzitic AlN were present.[10b,g] It is possible that the onset of poor adhesion in our films at $x > 0.5$ reflects the presence of both cubic and wurtzitic phases. Use of trimethylaluminum as a source leads to very efficient incorporation of aluminum into the film. For example, in depositions affording films of the composition $Ti_{0.83}Al_{0.17}N_{0.89}$, the concentration of titanium tetrachloride in the gaseous precursor stream was about 20 times that of trimethylaluminum, yet the ratio of titanium to aluminum in the film was 4.9. Interestingly, we were unable to deposit AlN films from trimethylaluminum and *tert*-butylamine in our hot-walled atmospheric pressure CVD system between 400 and 800 °C. This result is surprising, since Jones has reported the deposition of AlN films between 400 and 600 °C from trimethylaluminum and *tert*-butylamine in an atmospheric pressure CVD process using a cold-walled reactor.[19] It is possible that our hot-walled reactor leads to rapid particle formation during attempted AlN depositions with trimethylaluminum and *tert*-butylamine, as opposed to film formation. The cold-walled reactor used by Jones would favor surface reactions over gas-phase reactions, compared to a hot-walled reactor. Alternatively, the residence time of the reactants in our system may be insufficient to create the intermediates that lead to AlN films. The efficient incorporation of aluminum into titanium aluminum nitride films observed in our deposition system implies that trimethylaluminum reacts very readily with one or more intermediate species obtained by reaction of titanium tetrachloride with *tert*-butylamine. The X-ray diffraction spectra demonstrate that the TiN lattice is maintained in $Ti_{1-x}Al_xN$ and that progressive aluminum incorporation results through substitution of aluminum ions on titanium sites. Maintenance of a cubic rocksalt structure for $Ti_{1-x}Al_xN$ film up to at least $x = 0.5$ is typically observed in coatings that have been deposited by PVD and PACVD techniques.[10−13]

Analysis of the surface of our $Ti_{1-x}Al_xN$ films by XPS and RBS indicates that the surface is terminated largely by oxides, with Al_2O_3, TiO_2, and some TiN being observed. By contrast, RBS results demonstrate that the bulk of the film has low oxygen content. This situation is consistent with oxidation of the film surface upon exposure to ambient atmosphere. The increased resistance of our $Ti_{1-x}Al_xN$ films toward oxidation to TiO_2 at elevated temperatures under ambient atmosphere, compared to TiN films grown from titanium tetrachloride and *tert*-butylamine at 600 °C, almost certainly arises from the formation of a protective oxide layer on the surface of the film. Previous studies have also found that the surfaces of $Ti_{1-x}Al_xN$ films produced by PVD techniques and plasma-assisted CVD are terminated by aluminum oxides and have proposed that these oxides lead to the increased stability toward oxidation compared to TiN films.[10−13] The formation of an oxide-rich surface appears to be an intrinsic property of $Ti_{1-x}Al_xN$ films regardless of the method by which they are deposited.

The increased hardness of $Ti_{1-x}Al_xN$ films over TiN films has been a central motivation for investigation of this material. Presumably, the combination of increased hardness and increased stability toward atmospheric oxidation will lead to $Ti_{1-x}Al_xN$ replacing TiN as a hard coating for tool steel. We have measured the hardness of our films using nanoindentation and found that the hardness of $Ti_{1-x}Al_xN$ increases as x increases. The $Ti_{0.52}Al_{0.48}N_{1.38}$ film was 13% harder than a TiN film deposited on Corning 7059 glass at 600 °C using titanium tetrachloride and *tert*-butylamine as the source compounds. Our AFM images for a $Ti_{0.69}Al_{0.31}N_{0.85}$ film deposited on mica at 600 °C demonstrated that the average crystallite size (750 Å) was about 44% of the crystalline domain size in a TiN film deposited on mica under similar conditions (1700 Å). Since a decrease in grain size is typically accompanied by an increase in hardness,[19] the increase in hardness that we observe in our films probably results from decreased grain size compared to TiN. In a study that reported hardness values in units that can be directly compared to our results, it was found that the hardness of a series of $Ti_{1-x}Al_xN$ films ranged between 18 000 and 30 000 N/mm^2, with an average value of about 23 500 N/mm^2.[10c] These films were deposited using PVD techniques. These hardness values are substantially higher than what was observed for our films. The differences could have several origins. $Ti_{1-x}Al_xN$ films fabricated by PVD techniques typically possess preferred (111) orientations, but usually contain more than one orientation of TiN crystallites.[10] Films grown by plasma-assisted CVD typically reveal preferred (200) orientations,[12] but films

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(18) *Inorganic Phases*; JCPDS-International Centre for Diffraction Data: Swarthmore, PA, 1988.

(19) Jones, A. C.; Auld, J.; Rushworth, S. A.; Williams, E. W.; Haycock, P. W.; Tang, C. C.; Critchlow, G. W. *Adv. Mater.* **1994**, *6*, 229.

for which hardness values have been reported exhibited both (200) and (111) textures. By contrast, our films possess mainly (200) orientations. The crystallographic orientation and morphology of crystalline domains may be significant factors in film hardness. Smaller size domains may lower the measured hardness of the material. Finally, the density of our films may not be as high at that obtained in films fabricated by PVD methods, which would lead to lower hardness values.

Interest in ternary titanium nitride films in the electronics industry lies in the potential use of these materials as barrier layers to prevent the diffusion of aluminum or copper into silicon substrates.[8,13] TiN has been widely used as a barrier layer in microelectronics devices.[7,8] As mentioned above, the columnar structure of TiN can lead to barrier failure that occurs by metal atom migration along the grain boundaries. The $Ti_{1-x}Al_xN$ films reported here share the same well-ordered, columnar structure as TiN and presumably would fail in the same manner. The high resistivities of the $Ti_{1-x}Al_xN$ films would also negatively impact barrier performance.

In summary, we have developed a thermal CVD process for the fabrication of $Ti_{1-x}Al_xN$ films, using titanium tetrachloride, *tert*-butylamine, and trimethylaluminum as source compounds with a substrate temperature of 600 °C. The high growth rates, good film properties, inexpensive deposition equipment, and cheap, readily available precursors make our process attractive for the industrial fabrication of $Ti_{1-x}Al_xN$ films.

Experimental Section

General Considerations. Titanium tetrachloride, *tert*-butylamine, and trimethylaluminum were obtained from commercial sources. Titanium tetrachloride and trimethylaluminum were used as received. **Caution: Trimethylaluminum is pyrophoric and should be handled under an inert atmosphere by a skilled practitioner.** *tert*-Butylamine was dried over calcium hydride and distilled directly into a stainless steel bubbler. Corning 7059 glass, crystalline silicon, and mica were used as substrates for the film depositions. Glass substrates were wiped with a Kimwipe until visually clean. Mica substrates were freshly cleaved immediately prior to placement in the reactor. Silicon substrates were used as received.

X-ray diffraction was performed on a Rigaku Rotoflex powder diffractometer. X-ray photoelectron spectroscopy was performed on an SSX-100 ESCA spectrometer using Al Kα radiation ($h\nu = 1486.6$ eV). The binding energies were calibrated using Au $4f^7/_2 = 84.0$ eV. The Rutherford backscattering spectrometry analyses were carried out at the Michigan Ion Beam Laboratory, Ann Arbor, MI using a 1.7 MV Tandetron accelerator with 2.000 MeV $^4He^{2+}$ ions and $\theta = 90°$ ($Ti_{0.83}Al_{0.17}N_{0.89}$, $Ti_{0.52}Al_{0.48}N_{1.38}$) and −75.0° ($Ti_{0.69}Al_{0.31}N_{0.85}$). Sheet resistivity measurements were made using an R-Check four-point surface resistivity meter. Film hardness was measured by nanoindentation at the General Motors Technical Center using an instrument that has been previously described.[21] Scanning electron microscopy was conducted at the Glass Division of Ford Motor Company. AFM images were acquired using a home-constructed deflection-type microscope.[22] A quadrant photodiode detector was used to image both topographic and frictional force images simultaneously. The cantilevers were microlevers from Digital Instrument Co. with a force constant of 0.58 N/m. All images were taken under ambient laboratory conditions.

Atmospheric Pressure Chemical Vapor Deposition of $Ti_{1-x}Al_xN$ Films. The system used to fabricate the films is depicted in Figure 1. The reactor was comprised of a 2.5-cm diameter quartz tube situated in a Lindbergh tube furnace with a heated zone that was 35 cm long. Substrates were positioned in the center of the tube furnace and were supported on a steel stage. The liquid source compounds were loaded into stainless steel bubblers. The bubblers were maintained at 23 °C during film depositions. Nitrogen carrier gas was used to transport the precursor vapors to the reactor. The flow rate of carrier gas and consequently the amount of each source compound delivered to the reactor was controlled by a flowmeter. The concentration of each precursor in the total flow was calculated from the vapor pressures (titanium tetrachloride = 9.1 Torr at 20 °C; *tert*-butylamine = 298.2 Torr at 20 °C; trimethyaluminum = 8.7 Torr at 20 °C).[23] The source compounds were introduced to the reactor through a stainless steel injector consisting of three concentric tubes. The innermost tube delivered the titanium tetrachloride, while the outermost tube carried the *tert*-butylamine flow. For depositions of TiN, a separating flow of carrier gas was passed through the center tube of the inlet to prevent premature mixing of the precursors. To deposit $Ti_{1-x}Al_xN$ films, the separation flow was seeded with trimethylaluminum. The flow of gas through the reactor was regulated using four-port valves. The reactor was allowed to equilibrate at 600 °C under flow nitrogen carrier gas prior to film depositions. After equilibration, the four-port valves were turned to allow the flow of nitrogen gas through the bubblers, which resulted in passage of the precursors over the substrates. The precursor flow through the bubblers was continued for 180 s, and then the four-port valves were turned so that the precursor flow ceased and pure nitrogen gas flowed through the reactor. Nitrogen gas continued to flush the system while the films were cooled to ambient temperature. Film analyses are described in the text.

Hardness Testing. Nanoindentation hardness testing was conducted using a Hysitron TriboScope on TiN and three $Ti_{1-x}Al_xN$ films deposited on Corning 7059 glass at 600 °C. A Berkovich indenter made of diamond was used for indentation measurements. The procedure proposed by Oliver and Pharr for indenter shape calibration and data analysis was used to obtain the hardness values.[24] The indentation load was 2000 mN for all of the samples. This load resulted in an indentation depth of about 100 nm, which is in the range of 10% to 20% of the total film thickness. Therefore, the effects of the substrates are minimized.

Oxidation Study. Titanium aluminum nitride and titanium nitride films deposited on Corning 7059 glass at 600 °C were placed on a steel stage in a 2.5 cm diameter quartz tube that was open to ambient air at both ends. The tube was placed in a tube furnace and was heated for 3 h at temperatures of 550, 625, and 700 °C. The films were analyzed by X-ray diffraction before and after heating. For data, see the text.

Acknowledgment. C.H.W. and G.Y.L. are grateful to the National Science Foundation for support of this research. J.T.S. thanks the Institute for Manufacturing Research of Wayne State University for a fellowship.

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Rutherford backscattering spectrometry was performed at the Michigan Ion Beam Laboratory by Dr. Victor Rotberg. We are grateful to Dr. Yang-Tse Cheng and Jonathan Farr of General Motors Research for performing the hardness measurements.

Supporting Information Available: X-ray photoelectron and Rutherford backscattering spectrometry data for $Ti_{1-x}Al_xN$ films (11 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

CM990157U