Atmospheric Pressure Chemical Vapor Deposition of Titanium Nitride from Tetrakis (diethylamido) Titanium and Ammonia

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ABSTRACT

Titanium nitride (TiN) films were made from tetrakis (diethylamido) titanium (TDEAT) and ammonia by atmospheric pressure chemical vapor deposition (APCVD). Growth rates, stoichiometries, and resistivities were studied as a function of temperature and ammonia: TDEAT ratios. Films were characterized by four-point probe, Rutherford backscattering, forward (elastic) recoil, and x-ray photoelectron spectroscopies. TDEAT was found to have a higher deposition efficiency (>1/3), and slower reaction kinetics than the related $\mathrm{Ti(NMe_2)_4}$ (TDMAT) compound. Higher temperatures and relative $\mathrm{NH_3}$ concentrations were necessary to achieve similar growth rates. Though growth was slower than when using TDMAT, films from TDEAT had higher step coverage, lower resistivities (<1000 μΩ-cm) and were more stable with time. These films are promising candidates for diffusion barriers in 0.25 μm ULSI device technologies.

Introduction

Transition metal nitrides have metallic conductivity and refractory stability; these properties make them the materials of choice for diffusion barriers in microelectronic applications. Titanium nitride (TiN) is the most commonly used of these materials because of its low resistivity and resistance to chemical etches.

TiN is a conductive, chemically stable, hard material with gold-like optical properties. Its primary applications have been computer microcircuits, solar control coatings on windows, decorative jewelry and wear-resistant machine tools.[1] Early methods of deposition from titanium tetrachloride, nitrogen, and hydrogen (reaction 1)

$$\mathrm{TiCl_4} + \frac{1}{2}N_2 + 2H_2 \xrightarrow{900\text{-}1200^\circ\mathrm{C}} \mathrm{TiN} + 4\mathrm{HCl} \qquad [1]$$

required high temperatures that limited applications to highly refractive substrates, such as tungsten carbide machine tools. Kurtz and Gordon[2] lowered the deposition temperature to around 500°C by using preheated ammonia instead of nitrogen and hydrogen (reaction 2).

$$6\mathrm{TiCl_4} + 8\mathrm{NH_3} \xrightarrow{500^\circ\mathrm{C}} 6\mathrm{TiN} + 24\mathrm{HCl} + \mathrm{N_2} \qquad [2]$$

Though some substrates (*e.g.*, glass for solar control windows) can withstand these temperatures, silicon semiconductor wafers cannot be used except prior to the first stage of metallization. Additionally, chlorine incorporation into deposited films can cause corrosion of metal overlayers and reactor surfaces.

Physical vapor deposition (PVD) processes were developed to grow films on thermally sensitive substrates. The most popular PVD technique is reactive sputtering, which can be conducted at substrate temperatures below 300°C with deposition rates as high as 1 μm/min.[3] The high growth rates are a function of the sticking coefficient, which for sputtered ions is close to one. In high aspect ratio vias, however, a large sticking coefficient can generate retrograde structures and voids which lead to device failure. A collimator can improve ion directionality to enhance film conformality, at the expense of a greatly reduced deposition rate. As a diffusion barrier, though, PVD TiN compares poorly to CVD TiN.[4] While a thin layer of CVD TiN can protect silicon from a gold overlayer at 550°C,[5] PVD TiN fails at 350°C.[6] An 80 nm PVD film allowed more interdiffusion with aluminum than a 35 nm CVD TiN film under similar test conditions.[7] The push toward smaller dimensions makes the improved performance of CVD TiN crucial to the success of future generations of microchips.

Dialkylamido complexes of titanium offered solutions to the two problems plaguing TiN CVD: chlorine contamination of films and the high temperatures required for good film properties. The first problem is solved when chlorine is eliminated from the reaction chemistry. Growth temperatures are reduced because metal amido bond energies are 20 kcal/mol lower than metal-chlorine bond energies.[8] Fix *et al.*[9-11] and Musher and Gordon[12] were able to deposit TiN by reacting various alkyl-amido-titanium compounds with ammonia in an APCVD system. Others have used low pressure CVD systems.[13-15]

Much study has been devoted to the deposition of the $\mathrm{Ti(NMe_2)_4} + \mathrm{NH_3}$ system. Near stoichiometric TiN films have been grown below 350°C with low concentrations of impurities [C, O < 5 atomic percent (a/o)] and growth rates of 100 nm/min.[9-11] Films deposited with ammonia have poor conformality[12-15] as a result of their high growth rates. The improved conformality of films deposited from $\mathrm{Ti(NMe_2)_4}$ in the absence of ammonia has two side effects: slow growth and films were substoichiometric in nitrogen with high concentrations of impurities, specifically carbon and hydrogen.[12] Impurity incorporation produced highly resistive films that are not suitable for use in many microelectronic applications. The diethyl variant, $\mathrm{Ti(NEt_2)_4}$, or TDEAT, should be less reactive than TDMAT because of the steric bulk of the ethyl ligands. The decreased reactivity should lead to a lower sticking coefficient for the film precursor, and from there to improved conformality.[15]

We used TDEAT and ammonia to deposit TiN in an atmospheric pressure chemical vapor deposition system. Film growth, stoichiometry, and resistivity were studied as functions of deposition temperature and ammonia to TDEAT ratio. The results are compared to results obtained with $\mathrm{Ti(NMe_2)_4}$ and reviewed for diffusion barrier applications in 0.25 μm microelectronic technologies.

Experimental

Films were deposited in a Watkins-Johnson belt furnace described in a previous paper[12] under warm-wall (140-170°C) reactor conditions (see Fig. 1). This wall temperature was chosen to be high enough to prevent TDEAT condensation and low enough that the TDEAT would not thermally decompose. It was maintained by circulating and boiling deionized water through channels in the injector faceplate. Precursor gases were injected in an ABA

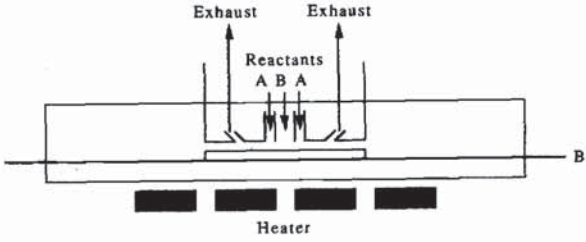

Fig. 1. Schematic diagram of belt furnace.

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configuration, with diluted ammonia passing through the center port (B) and diluted TDEAT through the outer two ports.

A prototype liquid delivery pump/vaporizer system developed by MKS Instruments was used to evaporate TDEAT (99.999%, Schumacher). The system limited the exposure of the TDEAT to elevated temperatures to just a few minutes, thereby reducing thermal decomposition in the evaporator. The heated vaporizer contained a pile of twenty sets of plates, each set comprised of one 2.5 cm diameter plate and one 3.2 cm diameter plate, compressed by a spring. The plates were 0.019 mm thick. Holes, 30 μm across and 14 μm apart, were etched into these plates. The metallorganic precursor was pumped under pressure to the vaporizer unit, where it seeped out between the plates and into the holes. The precursor evaporated as it was forced into these holes, through which nitrogen carrier gas passed at a rate of about 1 standard liter per minute (slpm). The maximum rate at which precursor can be vaporized is a function of the vaporizer temperature as well as the number of sets of plates used. The liquid density of TDEAT is 0.92 g/ml at room temperature.[16] Assuming full volatilization and ideal gas behavior for the vapor, 1.1 sccm of gaseous TDEAT was delivered to the reaction zone when pumping 20 μl/min of liquid. The vaporizer was maintained at 135°C and the delivery lines were kept at 150°C to prevent condensation. The pump, carrier gases, and ammonia were on for at least 20 min prior to deposition, in order to stabilize the delivery of vapor.

Semiconductor grade ammonia (99.995%) from Matheson was passed through a Nanochem resin purifier. The ammonia flow was set by a mass-flow controller. Nitrogen from a tank of liquid nitrogen was dried using Oxiclear and Nanochem purifiers. The flow rates of the nitrogen carrier gas flows were set by mass flow controllers or by calibrated pressure drops along small diameter tubing. The ammonia flow was typically diluted in 9 standard liters per minute (slpm) of nitrogen carrier gas. The TDEAT vapor mixture emerging from the vaporizer was also diluted by an additional 9 slpm of nitrogen carrier gas. The total flow rate of the gas mixture in the reaction zone was about 19 slpm, which is low enough so that laminar flow conditions should prevail (Reynolds number <30). Some turbulent mixing occurs, however, in the region below the injection slots.

Soda-lime float glass substrates from Kodak were used for most measurements. Crystal silicon substrates (p-type, <100>) from Silicon Sense were used for glancing angle and channeling RBS measurements. Patterned wafers for step-coverage measurements from SEMATECH had vias with aspect ratios of 1.9-2.5. The coated wafers were returned to SEMATECH for testing by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Step coverage values were defined as the ratio of film thickness at the bottom of a via to the thickness on the upper surface.

Samples were made in two ways, static and dynamic. In the static mode, the sample was preheated on the moving belt, and then stopped under the gas dispersion head during a timed deposition (typically 4 min), after which the belt drive was turned on again in order to move the sample out of the furnace. Dynamic samples were made with the sample moving steadily through the deposition zone. Static samples have a nonuniform thickness profile, increasing from zero at the center to symmetrically placed maxima in the upstream and downstream gas flows, and then decreasing to zero again past each of the exhaust slots. These nonuniform thickness profiles contain useful information about the gas flow dynamics and the chemical kinetics of the deposition reaction. Dynamic samples have a much more uniform film thickness over the whole substrate wafer, because each area of the wafer receives deposition from every part of the reaction zone.

The furnace has two belts, a primary one on which the deposition took place, and a secondary one onto which the wafer was transferred at a temperature of about 50-200°C, at which point it left the protective nitrogen atmosphere and entered the air. The use of two belts reduces the heat load on the primary muffle. The wafers cooled almost to room temperature on the secondary belt, which transferred them to the furnace exit. Their sheet resistances were first measured within a few minutes of their exit from the furnace, using a Veeco four-point probe (Model FPP-100). Subsequent sheet resistance readings were taken a few minutes later, a few hours later, and a few days later, in order to test the stability of the resistance values.

Rutherford backscattering spectroscopy (RBS) and forward recoil spectroscopy (FRS) data were calibrated with a Harwell Series I bismuth-implanted standard[17,18] and an a-Ge/c-Si sample with 3.7 a/o H (determined by hydrogen evolution).[12,19] Light atoms such as O, N, and C have smaller cross sections as well as smaller backscattering energies[20,21] and are difficult to detect quantitatively by RBS. Concentrations of these elements were determined by x-ray photoelectron spectroscopy (XPS) measurements and were calibrated with RBS data.[12] XPS carbon spectra were resolved into organic and carbide (metallic) peaks (see Fig. 2).

Sample thicknesses were determined by low-angle x-ray diffraction (XRD)[12,22-23] and by step profilometry on a step etched with a solution of equal parts of concentrated ammonia, 30% hydrogen peroxide, and deionized water.

Results

TiN was deposited for 4 min on 10 cm glass and 15 cm c-Si substrates. The resulting films were uniform in the direction perpendicular to the belt motion. To maximize the understanding of the process and to allow greater flexibility in examining the roles of process parameters: ammonia concentration, temperature, and total deposition time, the belt was held static during the deposition process. Selected sample conditions are shown in Table I.

The film thickness of the static samples varied in the direction of reactant flow. Deposition generally began approximately 5 mm from the site of ammonia injection and 3 mm from the location of introduction of TDEAT. Peak growth was observed at 18-24 mm from the center under most conditions. Film growth terminated below the exhaust ports at 36-38 mm.

Density.—The density of a thin film is a useful diagnostic of its structure. A density close to that of the bulk

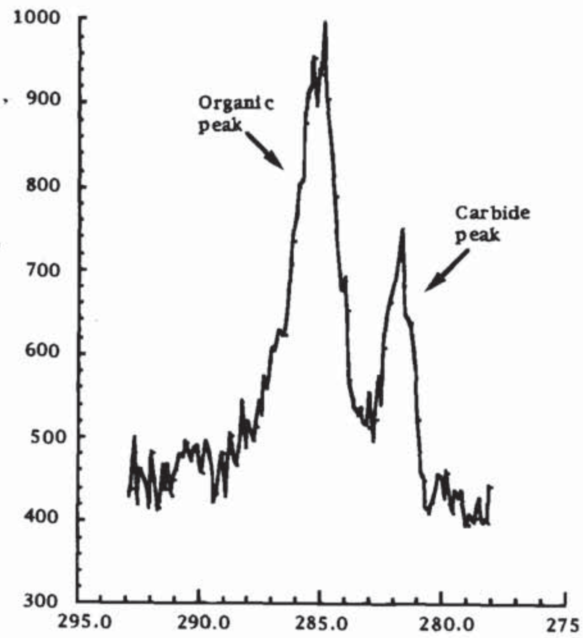


Fig. 2. XPS spectrum with organic and carbide carbon peaks resolved.

Table I.

T(°C)	NH_3/ TDEAT	Thickness (Å)	N/Ti	O/Ti	Organic C/Ti	Carbide C/Ti	H/Ti	Resistivity (μΩ–cm)
280	0	40	0.60	1.29	0.24	0.02	2.73	—
280	4	290	0.62	0.93	0.03	0.02	1.50	23000
280	30	350	0.90	0.81	0.01	0.04	1.20	4500
280	110	270	1.09	0.47		0.03	0.96	2010
370	0	80	0.60	0.72	0.35	0.09	2.72	—
370	4	530	0.84	0.52	0.03	0.05	1.34	2400
370	30	690	0.97	0.45	0.02	0.02	0.75	1310
370	110	580	0.97	0.46	0.00	0.02	0.65	930
420	0	160	0.62	0.67	0.34	0.08	2.42	39430
420	4	230	0.86	0.41	0.04	0.05	0.85	3690
420	30	270	0.93	0.47	0.02	0.02	0.45	2200
420	110	190	1.08	0.49	0.03	0.02	0.21	2490

All samples used 20 μl/min of liquid TDEAT, 1 standard liter per minute (slpm) of nitrogen carrier gas through the evaporator, diluted by an additional 9 slpm of nitrogen, and the ammonia was also diluted by about 9 slpm of nitrogen, for a total gas flow of about 19 slpm; deposition time was 4 min. Thickness were determined by RBS. Uncalibrated hydrogen to titanium ratios were determined by FRS data. Nitrogen, oxygen, and carbon concentrations were found by XPS, and the sensitivity calibration of the XPS was checked by RBS.

material suggests a compact, nonporous structure, while a lower density indicates a porous structure. One way to measure the density is to divide the mass per unit area by the thickness. The mass per unit area is readily measured by integrating the RBS spectra, and comparing with those measured for a calibrated bismuth-implanted standard.

The thicknesses have proven to be more difficult to measure reliably. Stylus profilometry has given widely scattered and unreliable values. Low-angle x-ray reflection did not give resolvable interference oscillations on static samples, because of their nonuniform thicknesses. Only dynamic samples with uniform thickness gave useful x-ray data (Fig. 3).

To find its density, a film was deposited under dynamic conditions in the furnace. The minimum belt speed of 0.75 in./min allowed for a 3 min growth period as the substrate passed through the deposition zone. An x-ray diffraction spectrum was collected from a film deposited at 370°C with NH_3/TDEAT = 32 (Fig. 3). Local extrema were fit to Eq. 3 to determine a film thickness of 18 nm. In Eq. 3 t is the film

$$\sin^2 \theta_n = \theta_c^2 + (n + \Delta n)^2 \lambda^2 / 4t^2 \quad [3]$$

thickness, λ is the x-ray wavelength, θ_n is the n^{th} minima/maxima, θ_c is the critical angle for total reflection, and $\Delta n = 1/2$ for a maximum and 0 for a minimum.[22] Simulations[23] of the x-ray reflection using this thickness agree reasonably well with the data (Fig. 3). Step profilometry provided similar results to the XRD data, but with larger errors. Data collected from RBS and XPS found an average stoichiometry of $TiN_{1.1}O_{0.4}C_{0.1}H_x$. From these data a film density of 2.5 g/cm^3 was calculated for this dynamic film. This value, significantly lower than literature values,[7] is also likely to be lower than those of most of our static samples, for the two reasons discussed below.

Film growth under dynamic conditions has two consequences for the film density. First, the deposited film includes layers deposited in every part of the deposition zone. This is important for the density because the unstable resistivity suggests that the film grown close to the exhaust is porous and less dense, as discussed below in the section on resistivity. This averaging of the dense and porous sections of the film leads to a low value for the dynamically deposited film. The second ramification is that dynamically deposited films are very thin, because of the short time during which they pass through the deposition zone. The absolute thickness is important because after the deposition the surface of TiN oxidizes into porous TiO_2. When the initial film is thin, the amount of material consumed by surface oxidation is large relative to the total thickness, and the average density of the film is reduced.

The remainder of the films in our study were deposited with the substrate stationary, so that any porous film near the exhaust is not sampled. Also, these stationary samples are thicker, because of the longer deposition times used. Thus the densities of the stationary samples are larger than those measured for the dynamic samples. For this reason, we used a literature value[7] of 4 g/cm^3 as the density for resistivity and thickness calculations.

Low temperatures (280°C).—APCVD of TiN from TDEAT is slow (1 nm/min) in the absence of ammonia.

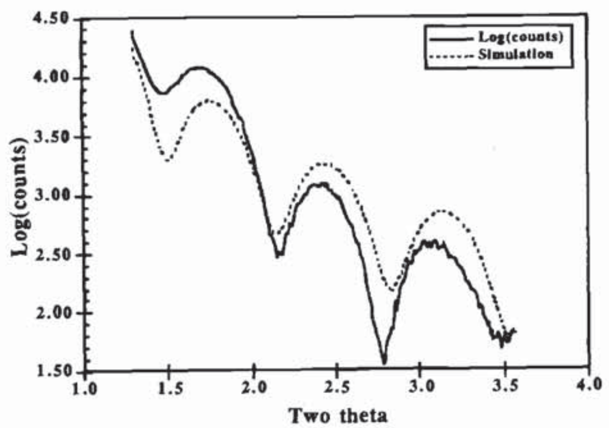


Fig. 3. Low angle X-ray diffraction spectrum of 180 Å TiN/c-Si.

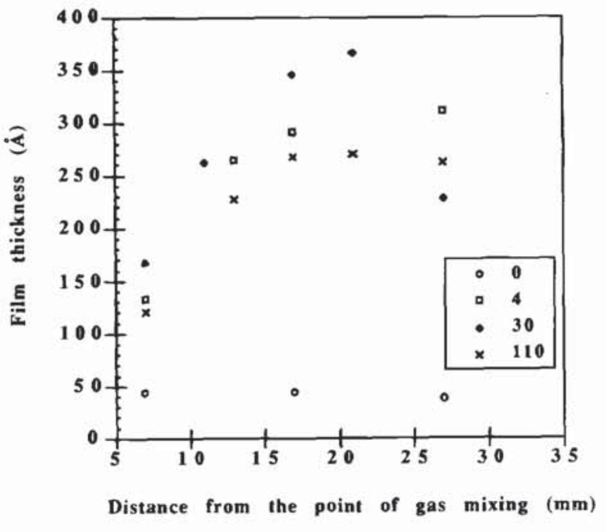


Fig. 4. Film thickness (Å) vs. distance from the point of gas mixing for different NH_3/TDEAT ratios at 280°C substrate temperature and four minutes of deposition time.

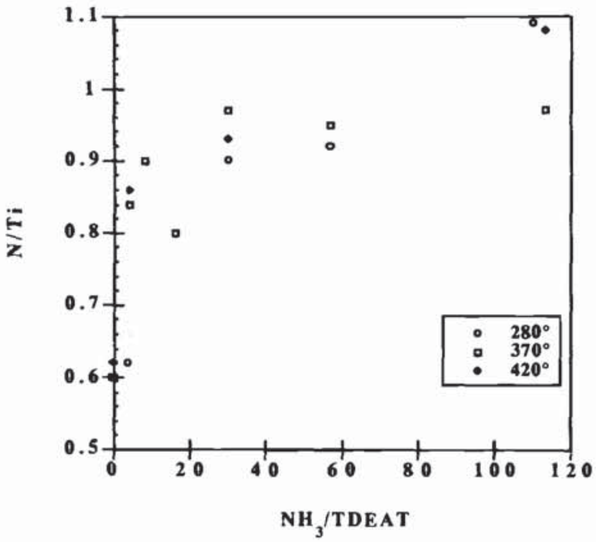


Fig. 5. Atomic ratio of N/Ti vs. NH_3/TDEAT ratios for deposition temperatures of 280-420°C.

Though thin, a 4 nm film could be seen as a tinting of the glass substrate. These nonstoichiometric (N/Ti = 0.6) films contained oxygen and carbon (O/Ti < 1.3, C/Ti = 0.26) and were nonconductive (sheet resistance > 10^5 Ω/□).

Adding 4 sccm of ammonia (NH_3/TDEAT = 4) to the reactant gas stream increased the film growth rate to 8 nm/min at the peak (Fig. 4). The carbon content fell to <5% relative to titanium. The oxygen to titanium ratio dropped to 0.9. The film resistivity decreased to 2.3 × 10^4 μΩ-cm.

The peak film growth rate was 9 nm/min when the ammonia flow was 30 times the flow of TDEAT. The growth rate was decreased when the ammonia concentration increased to 110 times the TDEAT concentration. The reduction in film thickness was seen in material deposited and was not due to an increase in film density.

Though peak growth rate declined at the highest NH_3 concentrations, other film properties improved. Films became near stoichiometric as the ammonia concentration increased (Fig. 5). Oxygen (Fig. 6) and hydrogen (Fig. 7) concentrations decreased, as did the resistivity (Fig. 8) when more ammonia was used. No trend was observed in the carbon data (Fig. 9).

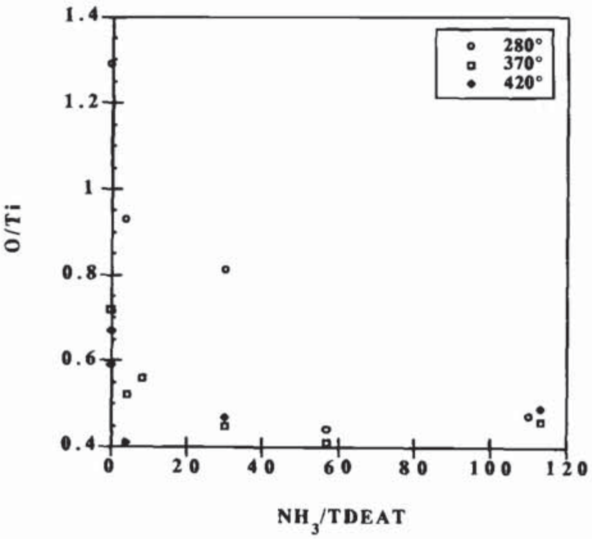


Fig. 6. Atomic ratio of O/Ti vs. NH_3/TDEAT ratios for deposition temperatures of 280-420°C.

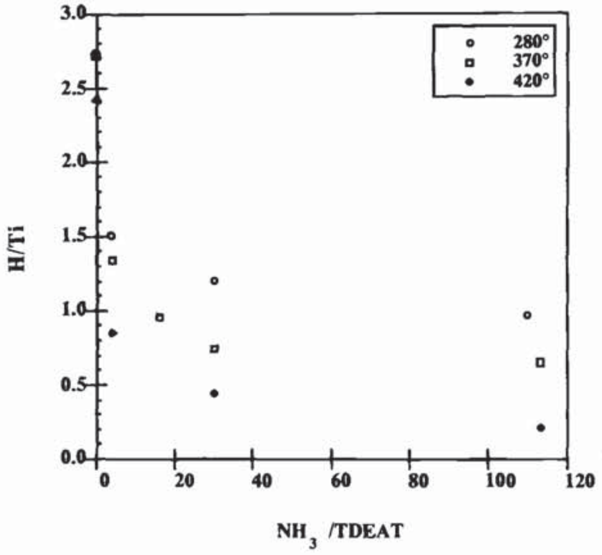


Fig. 7. Hydrogen content as a function of NH_3/TDEAT ratios for deposition temperatures of 280-420°C.

Intermediate temperatures (370°C).—The growth rate at 370°C without ammonia was 2 nm/min, double the rate at 280°C. While the nitrogen content remained constant, the ratio of oxygen to titanium fell and carbon concentration increased. Sheet resistance remained too high to measure.

Introduction of ammonia at this intermediate temperature increased the growth rate to 13 nm/min; however, excess ammonia concentrations above 0.18% reduced the film growth rate (Fig. 10). Stoichiometry improved as N/Ti increased to near unity at relative NH_3 concentrations over 20 (Fig. 5). Following the trends with increasing ammonia concentration observed at 280°C, the oxygen content decreased (Fig. 6), the hydrogen content decreased (Fig. 7), and carbon was virtually eliminated (<2 a/o) from the films made in an excess of ammonia (Fig. 9). Film resistivity decreased to 930 μΩ-cm when the ammonia/TDEAT ratio concentration reached 110 (Fig. 8). Resistivity was as low as 660 μΩ-cm for some films (at NH_3/TDEAT = 30) deposited at 370°C, the lowest values found in this study.

High temperature films (420°C).—At 420°C film deposited from pure TDEAT at 4 nm/min, double the growth rate

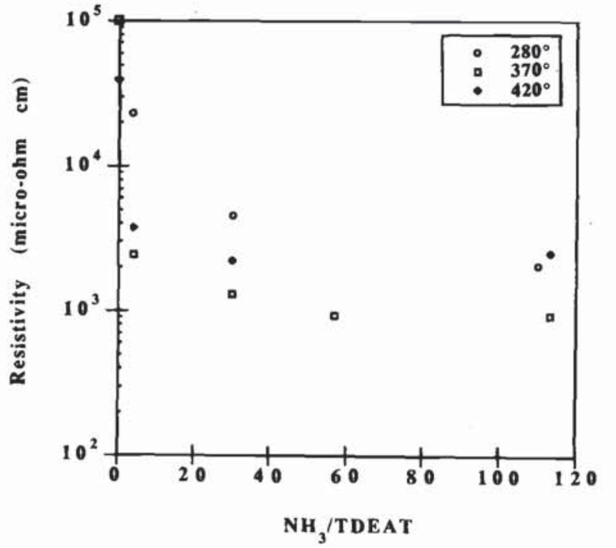


Fig. 8. Resistivity as a function of NH_3/TDEAT ratios for deposition temperatures of 280-420°C.

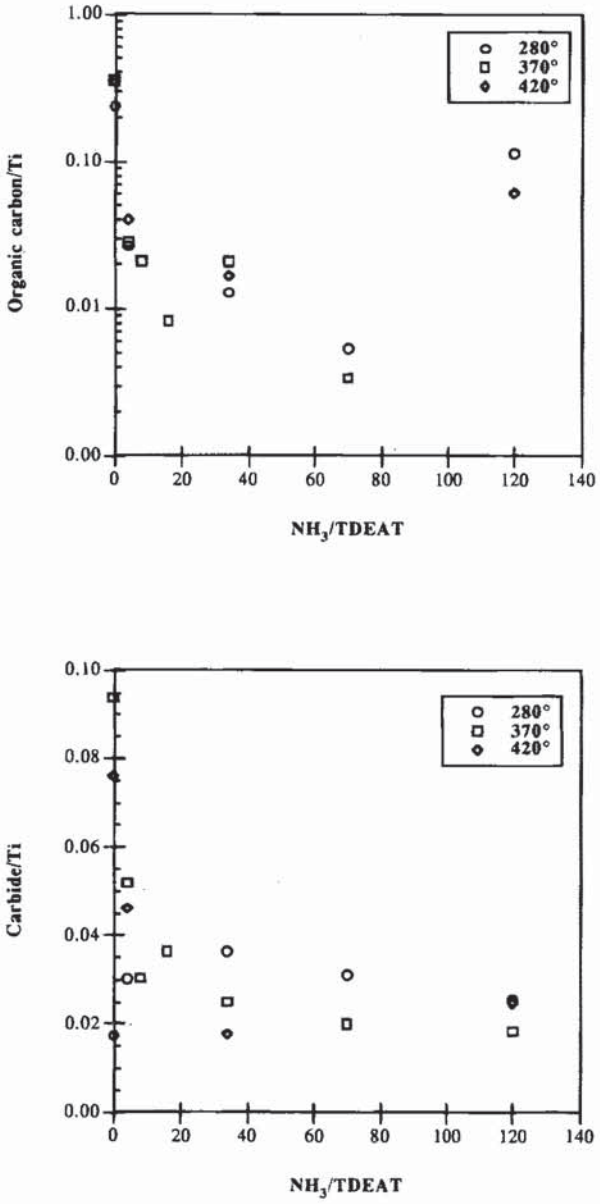


Fig. 9. (A, top). Atomic ratio organic C/Ti as a function of NH_3/TDEAT ratios for deposition temperatures of 280-420°C. (B, bottom) Atomic ratios of carbide C/Ti as a function of NH_3/TDEAT ratios for deposition temperatures of 280-420°C.

seen at 370°C. The nitrogen content remained at 60% of the titanium content. O/Ti decreased slightly, while the carbon content increased (C/Ti = 0.42-0.65). Film resistivity, not measurable on lower temperature films because of high sheet resistances, was 4×10^4 $\mu\Omega$-cm.

As at the lower temperatures, adding ammonia increased the nitrogen content to nearly stoichiometric values (Fig. 5) and decreased the hydrogen concentration (Fig. 7). The resistivity (Fig. 8) and carbon content (Fig. 9) decreased to their minima by a NH_3/TDEAT ratio of about 30. This resistivity (about 2×10^3 $\mu\Omega$-cm) is, however, higher than the values ($<10^3$ $\mu\Omega$-cm) obtained at 370°C. The lowest carbon content at 420°C (2 a/o) is also higher than that achieved at 370°C (<1 a/o). Little change in resistivity was observed (Fig. 8) for films made with still higher NH_3/TDEAT ratios (over 30).

Discussion

Mechanism.—Fix *et al.*[9] proposed that dialkylamido complexes decompose by two pathways: by β-hydride elimination (reaction 4)

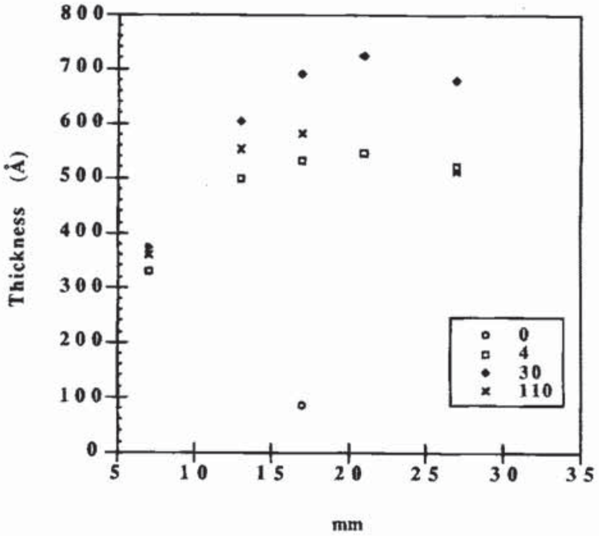
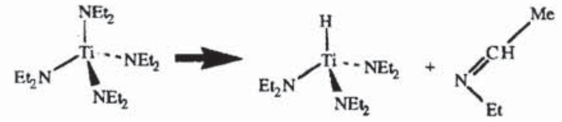
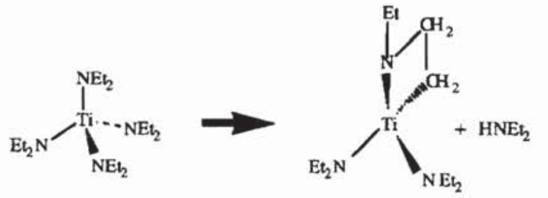


Fig. 10. Titanium coverage converted to thickness using a density of 4 g/cm³ vs. distance from the point of gas mixing for different ammonia/TDEAT concentrations at a substrate temperature of 370°C.



[4]

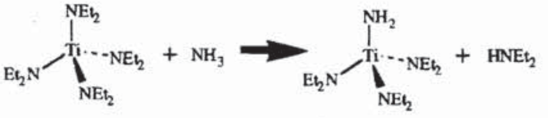
and by titanium insertion into a carbon-hydrogen bond to form a metallacycle (reaction 5)



[5]

This latter process may have a higher activation energy, which would account for the increase in carbon content with temperatures observed for films deposited in the absence of NH_3 (see Table I).

Ammonia can alter the reaction chemistry by transaminating the metal complex (reaction 6)[9]



[6]

This mechanism has been confirmed using IR spectroscopy and isotopic substitution in the analogous case of TDMAT.[14] In the presence of an excess of ammonia, successive transaminations then remove the remaining carbon-containing diethylamido ligands

$$(NH_2)Ti(NEt_2)_3 + NH_3 \rightarrow (NH_2)_2Ti(NEt_2)_2 + HNEt_2 \quad [7]$$

$$(NH_2)_2Ti(NEt_2)_2 + NH_3 \rightarrow (NH_2)_3Ti(NEt_2) + HNEt_2 \quad [8]$$

$$(NH_2)_3Ti(NEt_2) + NH_3 \rightarrow (NH_2)_4Ti + HNEt_2 \quad [9]$$

Film deposition may take place from these amido-titanium species, or they may decompose to other intermediates prior to film deposition.

Film growth rate.—CVD of TiN from pure TDEAT progressed slowly at 280°C. The film grew at 1 nm/minute. Raising the temperature to 370°C doubled the growth rate. The deposition profile thickened toward the end of the deposition zone, suggesting that a longer residence time would lead to a higher film growth rate. Thermal decomposition became somewhat faster at 420°C, where the growth rate doubled again to 4 nm/min of TiN. Film growth again increased toward the end of the gas-flow path.

Introduction of ammonia into the reactant stream increased the deposition rate (material accumulation) at all the temperatures studied. The effect was less pronounced at higher temperatures, where thermal decomposition contributed more significantly to film deposition. Ammonia concentrations above 0.18% (NH_3/TDEAT = 30) produced a 15 to 30% reduction in growth rate, possibly due to an increase in gas-phase nucleation and the formation of dust particles.

The deposition efficiency is defined as the number of titanium atoms deposited on the substrate surface divided by the number of titanium atoms incident into the reactor. The total number of titanium atoms deposited on the surface was calculated using the area densities found by RBS. Typically, five points were taken at 10, 16, 20, 24, and 30 mm from the center. The end points of deposition were found to be at 7 and 38 mm. Integration was performed using the trapezoidal rule.

The total amount of film deposited closely follows the trends described above for peak growth rates. The deposition efficiency approached 35% at 370°C using 33 sccm of ammonia and 1.1 sccm TDEAT in 19 slpm of nitrogen. Maximum efficiencies were observed when ammonia constituted 0.18% of the total flow for all temperatures. In the absence of ammonia, deposition efficiency increased from 3% at 280°C to 8% at 420°C.

Stoichiometry.—Pyrolytic decomposition of TDEAT produced substoichiometric films (N/Ti = 0.6) with high concentrations of carbon (C/Ti = 0.26-0.44), oxygen (O/Ti = 1.3-0.7), and hydrogen (Table I). TDEAT decomposed slowly below 300°C and low growth rates were observed. Higher temperatures provided more energy for the decomposition reactions with two consequences. First, the film growth rate increased because more reactive complexes nucleated on the substrate surface. Second, more carbide-like carbon was incorporated into the deposited film, because more carbon-titanium bonds were formed by reaction 5. Approximately 20% of the carbon in these films was carbide in character, corresponding to carbon bound directly to titanium. The remaining carbon was bound to nitrogen or other carbons (organic carbon), and presumably arises from the uncleaved ethylamido ligands.

Two factors contributed to the reduction in oxygen concentration observed in films grown at higher temperatures and with ammonia. Unlike crystal growth from a melt, where high growth rates generally lead to high impurity concentrations, in CVD high growth rates may result in higher purity films. High film growth rates and high purity are generally associated with an increase in the supply of the necessary reactants and a relative decrease in contaminants such as oxygen and water vapor. Low film growth rates occur when there is an undersupply of desirable reactants compared with contaminants in the gas, precisely the situation when depositing TiN in the absence of ammonia. Oxygen was incorporated into the film because the supply of activated precursor molecules is small relative to the oxygen concentration. Higher concentrations of activated precursor molecules are present when ammonia is used, reducing the relative contaminant oxygen concentration.

Additional oxygen may be incorporated when the films were exposed to air after deposition is completed. Initial exposure to air was at a temperature 50-200°C, followed by cooling to room temperature in air. Titanium dioxide has much higher electrical resistance than does titanium nitride. Evidence for additional oxidation after reaching room temperature is that some of the TiN thin films increased in sheet resistance with time. High ammonia concentrations and short gas residence times produced films showing little or no increase in resistance, and presumably less oxidation. More discussion of the resistances is given in the following section.

The hydrogen concentrations in the films decreased with temperature. The trend might be related to the evolution of hydrogen from TiH_2 reported by Chatbi *et al.*[24] in the temperature range 280-410°C.

The main effect of transamination (reactions 6-9) is elimination of diethylamine, presumed to be the primary source of carbon impurities. A small amount of ammonia removed 80% of the carbon present in ammonia-free films. Higher ammonia concentrations result in more complete removal of the diethylamido ligands and a reduction in carbon content to less than 5% of the titanium content. Hydrogen concentrations were also reduced with ammonia as a co-reactant, due to the transamination process which reduces the amount of hydrogen in the precursor by a factor of five.

As the transamination reactions remove carbon and hydrogen, nitrogen is retained more effectively in the films. As the nitrogen to titanium ratio increases, the resistivity decreases (Fig. 11). A similar relation between resistivity and stoichiometry was found for TiN films produced from TDMAT.[12] Conditions of high ammonia excess produce slightly overstoichiometric (N/Ti = 1.1 ± 0.1) films.[9-15,25-27]

Resistivity.—Resistivity, rather than sheet resistance, is used as a comparative characteristic because it is an intrinsic property of the material: the value should not depend on the dimensions of the sample. For thin films, however, resistivity may depend on the actual thickness of the film. Figure 12 shows the resistivity as a function of thickness for conditions, using ammonia TDEAT ratio of 30.

Film resistivity was reduced when NH_3 concentration was increased (Fig. 8). Sheet resistances of films deposited in the absence of ammonia at 280°C and 370°C were above 10^5 $\Omega/\square$, the upper limit of the four-point probe. (These points are above the scale of Fig. 8 and are not plotted.) Thermal decomposition of TDEAT at 420°C produced a film with a resistivity of 4×10^4 $\mu\Omega$-cm.

Small amounts of ammonia reduced film resistivities by an order of magnitude or more. One explanation for this effect is the dependence of resistivity on stoichiometry, specifically N/Ti ratio (Fig. 11). Another possibility is the hydrogen concentration, reported to be as high as H/Ti = 1 in some cases.[10,13] Hydrogen may affect the electrical properties of TiN (Fig. 13), and is reduced under high ammonia conditions. Ammonia may also influence film

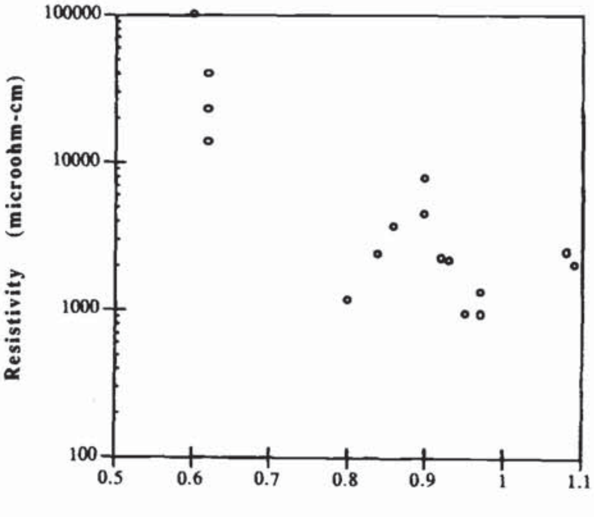


Fig. 11. Resistivity vs. atomic ratio of N/Ti.

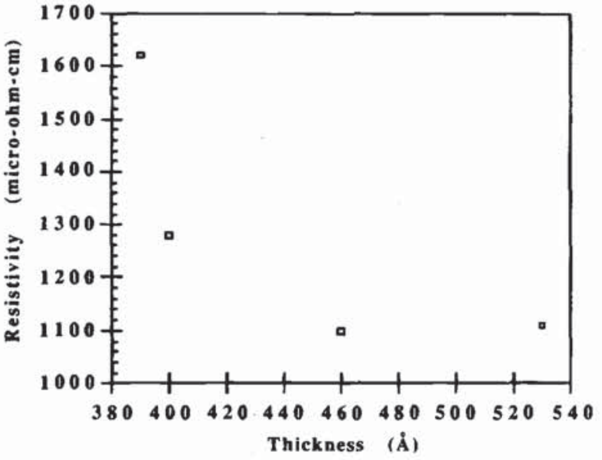


Fig. 12. Resistivity vs. thickness for films deposited at 370°C using 0.006% of TDEAT and 0.17% of ammonia.

densities; a denser film should have a lower resistivity. The lowest resistivities (660 μΩ-cm) were found at a deposition temperature of 370°C and high ammonia concentrations (NH_3/TDEAT = 110).

Resistivity also depended on oxidation of the film, which increased the measured sheet resistance. Though resistance was measured within 5 min of the substrate exiting the furnace, films were exposed to the atmosphere after exiting the primary muffle and before exiting the secondary (cooling) muffle. Because the exposure occurs at elevated temperatures (50-200°C), some oxidation may occur prior to the first resistance measurement. For some films, oxidation continued to increase the resistance even when standing at room temperature. These increases in sheet resistance occurred in a few minutes for films deposited from pure TDEAT, and over the course of hours for some films made from TDEAT with lower concentrations of NH_3. Films deposited from high ammonia concentrations were stable with time. Film areas deposited near the inlet region of gas mixing (short gas residence times) were usually stable, whereas areas formed near the gas exhaust (long gas residence times) were more likely to be unstable.

Dense films presumably absorbed less oxygen than porous (less dense) films and thus dense films have more stable resistances. We conclude that the stable, denser, and less porous films are formed from gas mixtures with high ammonia concentrations and short gas residence times. Higher ammonia concentrations should lead to more complete removal of the organic ligands, and hence to higher density, more stable, and lower resistance films.

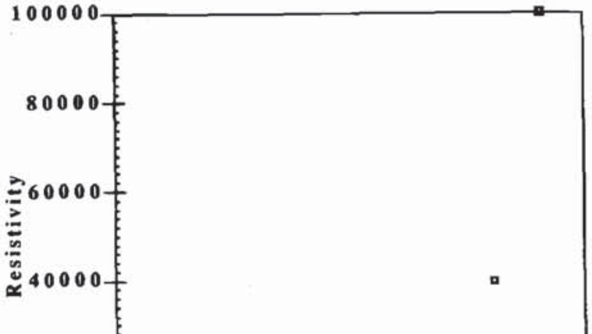


Fig. 13. Resistivity (μΩ-cm) vs. H/Ti.

Film deposited close to the gas inlet had stable resistances, while the resistances of some films deposited closer to the exhaust increased with time. The variation in stability suggests that the film deposited farther from the inlet had a more porous structure. Closer to the exhaust, the gas stream has reacted for a longer time, and may contain larger oligomers which result in porous film. Higher resistivities[27] as well as a reduction in stability result from lower film density. If diethylamido radicals are also formed in the reaction,[28] they would be present in greater numbers further from the inlet, and their readsorption might also contribute to the reduction of film density by occupying reactive surface sites.

Lower gas-phase concentrations of the titanium precursor should lower both the number of oligomers and the concentration of any radicals, thereby producing denser, more stable and lower resistance films. The present experiments did not test this prediction, because the same TDEAT concentration was used in all runs.

Step coverage.—A diffusion barrier must fully coat an underlying surface to protect it from deposited overlayers. Step coverage or conformality quantifies how well a deposited layer conforms to steps or irregularities on the substrate surface. Step coverage is defined as the ratio of the film thickness deposited at the bottom of a hole, to the thickness on the adjacent top surface. We grew films on wafers patterned with holes having aspect ratios of 1.9-2.5. These wafers were returned to SEMATECH for analysis by electron microscopy. SEM data were obtained for each set of growth conditions, and checked in a few cases with more reliable TEM data, which agreed within 20% with the SEM data.[29]

We expected that slower growing films would have higher step coverages than faster growing films: fast growth conditions are usually the result of high sticking coefficients which lead to low step coverage. A low sticking coefficient allows the incident molecule to bounce several times before adsorbing, leading to improved step coverage. Experimental results confirmed these expectations at lower temperatures (Fig. 14a and b): conditions that led to higher growth rates produced films with lower step coverages. Films deposited at the highest temperature, 420°C, did not, however, show any measurable trend of step coverage with growth rate.

TDEAT vs. TDMAT.—As expected from the similar reaction chemistries, the deposition of TiN from TDEAT/NH_3 is qualitatively similar to depositions from TDMAT/NH_3.[12]

The growth rates in the absence of NH_3 indicate similar pyrolytic decomposition rates of TDMAT and TDEAT, when the rates are corrected for the higher concentration of TDMAT used, assuming first-order dependence on the precursor concentration. Films grown from TDMAT without ammonia had higher nitrogen contents and lower impurity concentrations (O, C, H) than the corresponding films from TDEAT.

TiN films made from TDMAT required less ammonia to increase their growth rate, and their hydrogen content was reduced by smaller ammonia concentrations, compared to the corresponding TDEAT reactions. Stating this conversely, CVD of TDEAT requires higher ammonia concentrations to produce TiN films rapidly and with lowered hydrogen content. Also, TDEAT deposited TiN over the whole flow path from the point of mixing with ammonia to the exhaust slot (see Fig. 10). In contrast, TDMAT, under the same conditions, deposited most of its film in the first half of the flow path, on substrates near 400°C.[12] These observations show that the reaction rate of ammonia with TDEAT is slower than with TDMAT. This conclusion is supported by preliminary comparative measurements of

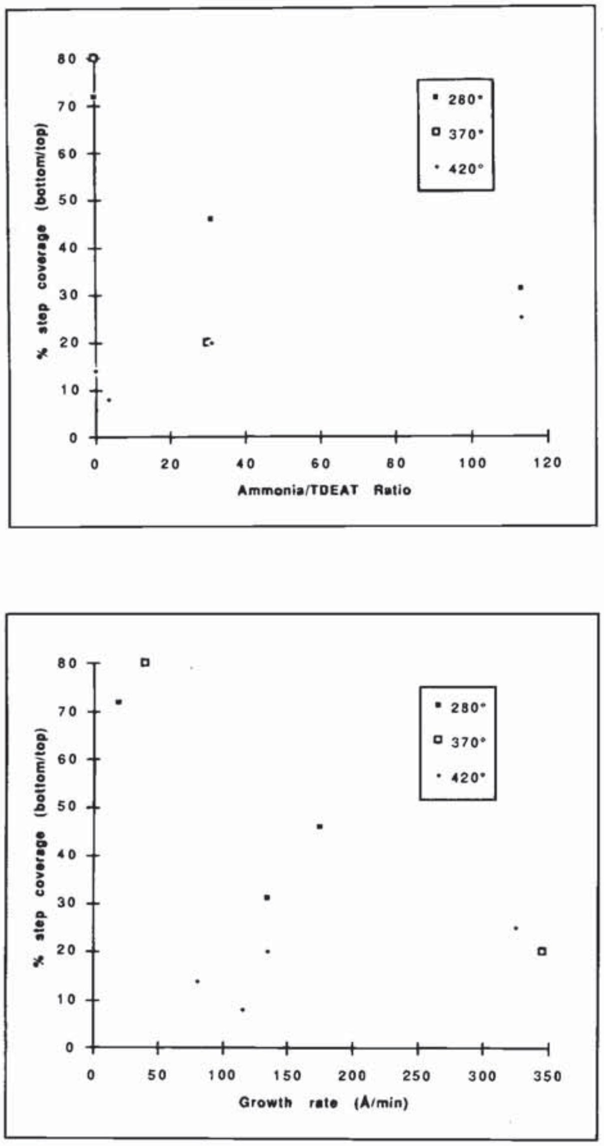


Fig. 14. (A, top) Film thickness at the bottom of a via divided by film thickness at the top of the via (step coverage) as a function of reactant ratio and deposition temperature. (B, bottom) Step coverage as a function of film growth rate (Å/min) and deposition temperature.

the rate of loss of these titanium precursors in a low-pressure gas-flow tube.[30]

The maximum conversion efficiency of TDEAT in the gas phase to titanium deposited in the film was 35%, whereas the maximum conversion efficiency for TDMAT was only 14%. This may result from the higher sticking coefficient of intermediates generated by reaction of TDMAT with ammonia, which more easily nucleate homogeneously as dust particles. Deposition of TiN from TDMAT and ammonia produced a thick layer of powder on the bottom surface of the reactor, whereas very little powder was produced by the TDEAT reaction. These observations suggest that much of the reactive TDMAT formed dust particles, while the less reactive TDEAT remained available to deposit film on the substrate.

Comparison to other deposition techniques.—APCVD growth rates were low relative to the 1000 nm/min attainable by reactive sputtering.[3] However, use of a collimator, necessary to reactively sputter into high aspect ratio structures, reduces growth to rates comparable with CVD growth rates. LPCVD processes can deposit films at rates as high as 100 nm/min,[26] although lower rates (1-10 nm/min) generally lead to better film qualities.[13,25] High deposition rates are often achieved by using a high precursor flow rate. In this work, films grew at a rate of 9-15 nm/min using a very low flow of only 1 sccm of TDEAT vapor.

Summary

Titanium nitride thin films have been fabricated by the atmospheric pressure chemical vapor deposition of $Ti(N(C_2H_5)_2)_4$ and NH_3. Films uniform over 150 mm substrates were grown in a belt furnace open to laboratory atmosphere at both ends of the muffle.

Pyrolytic decomposition of pure TDEAT without NH_3 yielded substoichiometric titanium nitride films ($N/Ti = 0.6$). The high concentrations of impurities ($C/Ti = 0.25$-0.65; $O/Ti = 0.7$–1.3) were due to incomplete elimination of diethylamido ligands, low growth rates (1–4 nm/min), and post-deposition oxidation. The nonstoichiometric character of these films produced high resistivities.

Near stoichiometric TiN ($N/Ti = 1.0 \pm 0.1$) films were produced over a broad range of temperatures (280–420°C) and ammonia concentrations ($NH_3/TDEAT = 4$–110). Chemical composition was weakly sensitive to process parameters with the exception of hydrogen, which continued to decline with increases in ammonia and/or temperature. Nitrogen contents increased slightly with ammonia partial pressure, while the oxygen concentration decreased as N/Ti increased. Carbon contamination was below 5 a/o when ammonia was used as a co-reactant.

Growth rates were somewhat insensitive to ammonia concentrations. Peak deposition rates required $NH_3/TDEAT = 30$. A factor of 4 difference in ammonia concentrations reduced film growth rate from this maximum by 15–30%. Film growth was a function of deposition temperature, attaining maximum values (18 nm/min) at 370°C. Deposition rates were 50% lower at 280 and 420°C.

Low-resistivity films (930 $\mu\Omega$-cm) were grown with high ammonia concentrations ($NH_3/TDEAT = 110$) and intermediate temperatures (370°). The low resistivities observed under high ammonia conditions are probably due to the observed increase in nitrogen content with ammonia partial pressure. Higher ammonia concentrations might further lower resistivities at the expense of deposition rates. Stable, dense films were obtained at high ammonia concentrations and at short gas residence times.

Step coverages as high as 80% were achieved, though under conditions which produced high resistivities. As a compromise, films with 2400 $\mu\Omega$-cm resistivities can be grown with 50% step coverage in holes with an aspect ratio of about 2.

Conclusions

APCVD of TiN from TDEAT and ammonia is slower and more responsive to deposition parameters than APCVD from TDMAT and ammonia. Precursor to film conversion rates, which are around 35% in the presence of ammonia, are comparable to LPCVD techniques and provide wide latitude for large-scale manufacturing processes. Process flexibility allows adjustment of growth conditions to optimize film characteristics. Further studies are in progress to assess the applicability of this process to the production of diffusion barriers in the next generation of ULSI technologies.

Acknowledgments

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A 0.25 μm MOSFET Technology Using *In Situ* Rapid Thermal Gate Dielectrics

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ABSTRACT

A 0.25 μm (MOSFET) technology using 6.5 nm thick *in situ* rapid thermal gate dielectrics, including RTO, RTCVD, and RPECVD was designed for channel length of 0.18 ± 0.06 μm and evaluated experimently. Devices with L_{eff} down to 0.17 μm were fabricated using the different dielectrics and electrically characterized. In addition to the RTP dielectrics, the technology features a LOCOS isolation having small bird's beak (45 nm), very shallow source/drain junction and extension depths (70 and 30 nm, respectively) with very low gate induced drain leakage (GIDL). The key technology elements such as isolation, channel dopant redistribution, polysilicon gate patterning, and shallow junction formation are discussed along with the impact of the different dielectrics on device characteristics.

Introduction

The continued scaling down of metal oxide semiconductor (MOS) devices is putting more and more stringent requirements on traditional batch (Furnace) processing, such as the control of manufacturing environment, equipment costs, and low-thermal budget processing. *In situ* single-wafer rapid thermal processing (RTP) is being considered as an alternative to batch (Furnace) processing, mainly because of its well-controlled environment by using multifunction cluster tools,[1] reduced fabrication cost through processing large wafers,[2] and enhanced flexibility for manufacturing numerous products based on different technology.[3] RTP is also shown to have a great advantage in terms of achieving low thermal-budget processing.[4,5] Based on the concept of single-wafer processing, several *in situ* rapid thermal gate dielectric processes have been developed, including rapid thermal oxidation (RTO), rapid thermal chemical vapor deposition (RTCVD), and remote plasma enhanced chemical vapor deposition (RPECVD). By optimizing the process conditions, it has been demonstrated by many researchers that these dielectrics have comparable properties such as breakdown voltage and interface charge density to furnace oxides.[6-9]

To further study the feasibility of using these rapid thermal dielectrics as high-quality thin gate dielectrics in deep submicron technology, 0.25 μm MOSFETs were designed

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