ADVANCED MATERIALS FOR OPTICS AND ELECTRONICS, VOL 6, 135–146 (1996)

Review Paper

Filament-activated Chemical Vapour Deposition of Nitride Thin Films

Sadanand V. Deshpande,* Jeffrey L. Dupuie† and Erdogan Gulari*
Department of Chemical Engineering and Center for Display Technology and Manufacturing, The University of Michigan, Ann Arbor, MI 48109, U.S.A.

We have applied the novel method of hot filament-activated chemical vapour deposition (HFCVD) for low-temperature deposition of a variety of nitride thin films. In this paper the results from our recent work on aluminium, silicon and titanium nitride have been reviewed. In the HFCVD method a hot tungsten filament (1500–1850 °C) was utilised to decompose ammonia in order to deposit nitride films at low substrate temperatures and high rates. The substrate temperatures ranged from 245 to 600 °C. The film properties were characterised by a number of analytical and optical methods. The effect of various deposition conditions on film properties was studied. All the films obtained were of high chemical purity and had very low or no detectable tungsten contamination from the filament metal.

KEYWORDS hot filament chemical vapour deposition; CVD; high-rate deposition; ammonia; silicon nitride; aluminium nitride; titanium nitride

INTRODUCTION

Hot filament-activated chemical vapour deposition (HFCVD) is a simple and a relatively inexpensive method that has been used to deposit a variety of materials. In this method a resistively heated filament (tungsten, rhenium or tantalum) is used to thermally and/or catalytically dissociate one or more of the source gas molecules to produce reactive precursors needed to form the desired film. One of the most attractive features of the HFCVD approach is that the thermal activation of reactants is decoupled from the film growth step at the substrate. This simple approach allows for deposition at low substrate temperatures (from room temperature to 400 °C). High film deposition rates can be obtained by appropriately adjusting the deposition conditions. Using proper reactor design and operating regimes, films with varied properties can be deposited with little or no contamination from reactions at the reactor walls as is found in other techniques such as plasma-assisted chemical vapour deposition.

HFCVD has been extensively used for over a decade to deposit polycrystalline diamond thin films.[1-3] Polycrystalline diamond has been deposited on a number of different non-diamond substrates using a variety of carbon-containing gases and under varying conditions in a hot filament system. However, typical conditions under which good quality, highly faceted diamond is obtained are: filament temperature, 2000–2200 °C; filament-to-substrate distance, 1.0 cm; substrate temperature, 800–1000 °C; reactor pressure, 20–30 Torr; gas composition, 0.5% CH_4 in hydrogen. This simple technique has provided great insight into the process chemistry and the mechanism of diamond

* Corresponding authors.
† Present address: Automotive Components Division, Ford Motor Company, Dearborn, MI 48120, U.S.A.

CCC 1057–9257/96/030135–12
© 1996 by John Wiley & Sons, Ltd.

Received 30 August 1995
Accepted 13 October 1995

deposition. Chemistry in an HFCVD process has been the subject of several experimental[4–6] and theoretical studies.[7–9] It is now well recognised that methyl radicals in the presence of a supersaturation of hydrogen atoms are responsible for the deposition of diamond. The H atoms, generated owing to the high filament temperatures, help to remove any sp^2-bonded carbon (which can form graphite) and also help in growth of the sp^3 diamond phase by hydrogen abstraction from a surface-bonded methyl group. The hydrogen atoms also transport a significant amount of energy[10] to the diamond growth surface through the recombination reaction ($H + H = H_2$; $\Delta H = -104$ kcal mol^{-1} of H_2).

One of the early attempts at producing thin films of various silicon alloys, at low temperatures using HFCVD, was reported by Matsumura.[11] In that work the results for the deposition of amorphous silicon, silicon–germanium, silicon nitride (using ammonia and HF_3) and silicon carbide were presented. In another study Matsumura[12] reported the deposition of good quality silicon nitride films from silane and hydrazine (with nitrogen as the carrier) at low substrate temperatures (230–370 °C). The tungsten filament temperatures were varied from 1180 to 1390 °C and deposition rates as high as 300 Å min^{-1} were obtained. Near-stoichiometric silicon nitride (N/Si ratio ≈ 1.33) films could be deposited at higher H_2H_4 partial pressures with little or no oxygen in the film bulk. Yasui *et al.*[13] have obtained silicon nitride films using monomethylamine and silane as precursors. In that study hydrogen was decomposed over the hot filament (2400 °C) which was then allowed to react with the other process gases, fed further downstream from hydrogen. The use of a hot filament provided deposition rates of about 1000 Å min^{-1}, which were about an order of magnitude higher than those for conventional thermal CVD of silicon nitride.

The other nitrides that have been deposited by HFCVD are those of boron,[14] gallium,[15] aluminium[16] and titanium.[17] The hexagonal phase of boron nitride[14] was deposited from a single-source precursor (borazine) at temperatures ranging from room temperature to 400 °C. Polycrystalline gallium nitride[15] was deposited epitaxially, layer by layer, on a rotating substrate and by utilising a novel gas flow design. Our research group has demonstrated the feasibility of depositing aluminium[16] and titanium[17] nitrides.

In several other studies HFCVD has been used for the deposition of device quality hydrogenated amorphous silicon.[18–22] Wiesmann *et al.*[18] were the first to report the use of HFCVD for depositing amorphous silicon (a-Si:H) from pure silane at a total pressure of about 0.4 mTorr. In that study they used tungsten or carbon filaments (heated to 1600 °C) to obtain a-Si:H films with high photoconductivity. Matsumura[19] used the catalytic properties of a tungsten filament ($T_{fil} = 1000–1500$ °C) to obtain a-Si:H films at large deposition rates (~20 Å sec^{-1}) and with high photosensitivities (photo-/dark conductivity ratio ≈ 10^5). Doyle *et al.*[20] have shown that for a filament temperature of 1300–1400 °C and substrate temperature of 180–240 °C, very high deposition rates of up to 600.0 Å min^{-1} could be obtained. The properties of a-Si:H produced by HFCVD were comparable with those of films made by the glow discharge method. Mahan *et al.*[21] have shown that device quality a-Si:H films containing very low bonded hydrogen (~1%) can be deposited by the hot filament method at 550 °C. It should be mentioned here that typical device quality amorphous silicon films deposited by conventional plasma-enhanced CVD have about 10% bonded hydrogen. In a recent study[22] the optoelectronic properties of a-Si:H films made by HFCVD have shown a strong dependence on substrate temperature. As substrate temperatures increased from 190 to 220 °C, the optimal (Tauc) band gap increased from 1.9 to 2.3 eV while the photo-/dark conductivity ratio remained essentially constant at 10^5. For temperatures between 220 and 250 °C the band gap decreased to 1.8 eV and the photo-/dark conductivity ratio decreased to 1.0, whereas for temperatures about 250 °C the band gap further decreased to 1.7 eV and the ratio remained unchanged at 1.0.

In the past few years we have extended the HFCVD system for deposition of a variety of films: silicon nitride,[23–26] aluminium nitride,[16,27] titanium nitride,[17] boron carbide[28] and polycrystalline silicon.[29] We have also successfully applied this technique for etching/cleaning of gallium arsenide substrates with hydrogen chloride as the etch gas.[30] In this paper we discuss the results from our work on the deposition of aluminium, silicon and titanium nitrides. We have evaluated the properties of these films using a variety of analytical and optimal techniques. The results for each of these nitrides will be presented under separate sections. The experimental system used in these studies is described in the next section.

EXPERIMENTAL

The details of the experimental set-up have been described elsewhere.[31,32] The nitride films were deposited in a 6 inch, six-way-cross stainless steel reactor. A stainless steel cooling water line brazed to the exterior of the reactor provided cold wallop-eration. Substrates (2 inch diameter) were pressed on to the susceptor by molybdenum clamps. The susceptor was heated by two 300 W cartridge heaters and the temperature was measured by a thin wire Pt–Rh (Type C) thermocouple clamped to the susceptor surface. The filament assembly consisted of a 0.25 mm diameter tungsten wire wrapped around 13.0 mm diameter quartz rods, supported by stainless steel sleeves. The filament assembly was placed about 4.0 cm from the substrate. The filament temperature was monitored by an optical pyrometer (disappearing filament type) through a glass viewport on the chamber. This measurement gave a temperature accuracy of about 50 K.

The gases were fed into the reactor by MKS mass flow controllers. The substrates faced downwards during film growth to mitigate dust contamination. Reactants flowed into the reactor through either of two feed lines, one of which consisted of a gas dispersal ring. In this arrangement the ammonia flowed over the filament and the other source gas (with hydrogen as diluent) was fed through the gas dispersal ring. The gas dispersal ring was placed between the filament and the substrate. This configuration minimised film growth on the filament assembly. The deposition pressure was measured by a capacitance manometer and controlled by a throttle valve. The reactor gases were pumped using a Roots blower backed by a rotary vane pump.

SILICON NITRIDE

Amorphous silicon nitride (a-SiN_x:H) films are used in integrated circuit manufacture as oxidation masks, gate dielectrics, interlevel insulators and final passivation layers. Conventionally, Si_3N_4 thin films are deposited at high substrate temperatures (700–900 °C) by thermal CVD and at low temperatures (200–400 °C) using plasma methods.[33,34] Low-temperature deposition of silicon nitride is particularly important in compound semiconductor technology as a passivation and capping material and in processes where thermal budgeting is critical. The major problem in conventional low-temperature depositions is the high amount of hydrogen incorporation (10%–30%) in the films, which leads to high etch rates (up to 2500 Å min^{-1}) in buffered HF solutions.[35] In this paper we summarise our work on the use of the hot filament-assisted CVD technique for deposition of silicon nitride thin films at high rates, low hydrogen content and low substrate temperature with disilane and ammonia as reactants.

The deposited films were characterised by ellipsometry, infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The film thicknesses and refractive indices were measured by an ellipsometer at 632.8 nm and averaged over at least 10 measurements. The target thickness of these films was 2600–2900 Å (second blue–green colour under fluorescent light) in order to obtain an accurate determination of refractive index by ellipsometry. Transmission Fourier transform infrared spectroscopy was used to determine the bonding configurations and estimate the hydrogen content in the films using the method of Lanford and Rand.[36] The film composition was determined by XPS as a function of depth by 3.0 keV argon ion sputter profiling. The sensitivity factors provided by the XP spectrometer software were used for elemental analysis without further calibration. The optical band gap (Tauc) of these samples was measured by depositing the films on fused silica substrates and then determining the absorption coefficient using a UV–visible spectrometer.

The effects of several deposition parameters on film properties were studied. The results are summarised in Table 1. In the first set of experiments the disilane flow rate was varied from 1.1 to 3.2 sccm. The film refractive index also increased from 1.86 (film 1) to 2.42 (film 4). This was due to a depletion of nitrogen-containing species in the vicinity of the substrate with a higher disilane flow. A high deposition rate of about 1700 Å min^{-1} was obtained for a disilane flow rate of 3.2 sccm. XPS sputter depth profiling of film 4 indicated that this film was silicon-rich, with a bulk Si/N ratio of 1.8. The composition of film 2 was closer to stoichiometric Si_3N_4, with a bulk Si/N ratio of 0.95. Oxygen was detected only in the top 10 nm of the film and not in the film bulk, indicating that the films were dense and there was no detectable oxygen incorporation from the reactor ambient. Fig. 1 shows the transmission

Table 1. Effect of experimental parameters on a-SiN_x:H film deposition rate and refractive index

(a) Effect of disilane flow and filament temperature; reactor pressure 0.5 Torr, carrier gas flow (H_2) 230 sccm, substrate temperature 375 °C, ammonia flow 80 sccm

Film	Disilane flow (sccm)	Filament temperature (°C)	Deposition rate (Å min^{-1})	Refractive index
1	1.1	1700	1119.8	1.86
2	1.6	1700	1445.3	1.95
3	2.1	1700	1716.8	2.03
4	3.2	1700	1680.3	2.42
5	1.6	1500	611.7	2.08
6	1.6	1600	1099.2	2.02
7	1.6	1850	1675.7	1.87

(b) Effect of composition of disilane carrier gas; T_{sub} = 375 °C, T_{fil} = 1700 °C, total carrier gas flow 142 sccm, ammonia flow 80 sccm, reactor pressure 0.5 Torr

Film	Hydrogen flow (sccm)	Argon flow (sccm)	Deposition rate (Å min^{-1})	Refractive index
8	142	0	1454.4	1.93
9	71	71	1186.1	1.94
10	0	142	954.8	2.02

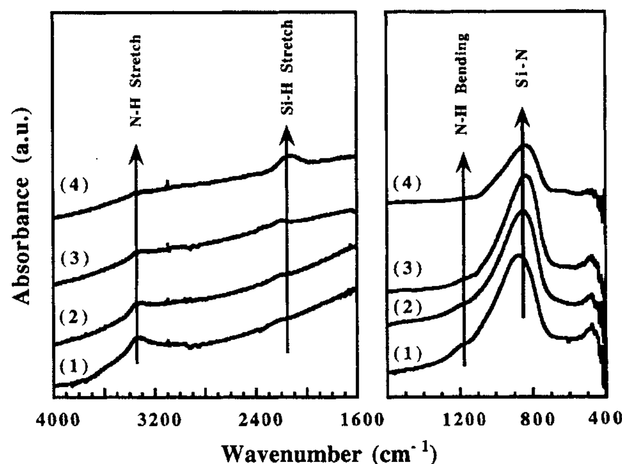

Fig. 1. Transmission FTIR spectra of silicon nitride films. The N–H and Si–H stretching regions have been expanded for clarity

FTIR spectra of these films. It may be noted that as the refractive index increases, i.e. the silicon content in the films increases, the absorption in the N–H stretching mode (~3350 cm^{-1}) decreases and that in the Si–H stretching mode (~2150 cm^{-1}) increases. Also, the shoulder in the Si–N asymmetric stretching peak (~840 cm^{-1}) obtained owing to N–H bending (~1175 cm^{-1}) decreases from film 1 to film 4. This indicates that as the films become silicon-rich, the population of hydrogen-terminated dangling bonds shifts from nitrogen to silicon. The total bonded hydrogen content in these films was determined to be low and was less than 6×10^{21} atoms cm^{-3}. This is a definite improvement over conventional low-temperature deposition methods such as plasma CVD.[34]

In the second set of experiments the filament temperature was varied between 1500 and 1850 °C for a disilane flow rate of 1.6 sccm and a hydrogen flow rate of 230 sccm. An increase in filament temperature would produce more of the nitrogen precursor species, possibly NH radicals, in the reactor ambient and would therefore increase the film deposition rate, as was seen in these experiments. On the other hand, the film refractive index decreased owing to a combination of two effects: an increased amount of activated nitrogen species and a limited supply of disilane.

In the third set of runs (films 8–10) the composition of disilane carrier gas was varied to study its effect on film deposition rates. The total carrier gas flow rate was 142 sccm, the disilane flow rate was 1.1 sccm and the filament temperature was held at 1700 °C. Asseen in Table 1 (section (b)), the deposition rate of the films decreases with increasing argon fraction in the carrier gas. Also, the refractive index of films 8–10 increased, indicating a decrease in nitrogen-containing species, with increased argon dilution of the carrier gas. The decomposition of ammonia on a hot platinum filament (>1000 °C) has been studied with laser-induced fluorescence by Selwyn and Lin[37] under pressure conditions similar to those used in the study. Their results indicated that the rate of NH radical production by catalytic action of the filament increased with increasing filament temperature and also with addition of hydrogen to the gas mixture. The addition of hydrogen is believed to enhance the desorption rate of NH radicals from the filament surface. In this study argon dilution of the hydrogen carrier gas may have caused a decrease in NH radical desorption rate, leading to a decreased film deposition rate.

In addition to these parameters, the substrate temperature was also varied to evaluate its effect on the hydrogen content and etch rate of the films. These results are given in Table 2. It should be noted that in spite of the high deposition rate, the films deposited by HFCVD are very dense and show very low etch rates in a buffered hydrofluoric acid (BHF) solution when compared with plasma-deposited (PECVD) films. We have also measured the optical band gap of these films. Fig. 2 shows the variation in band gap as a function of disilane flow rate. The band gap of the films can be changed by adjusting the disilane flow rate. The band gap decreases with increasing disilane flow, because the films become increasingly silicon-rich.

The dielectric response of silicon nitride films was measured by spectroscopic ellipsometry and compared with a theoretical model.[24] The model that showed the best fit to the experimental dielectric response of the films consisted of three layers: a top thin surface layer of silicon dioxide, followed by a slightly silicon-rich silicon nitride layer with a small fraction of voids, then a bottom layer of interfacial oxide between the deposited film

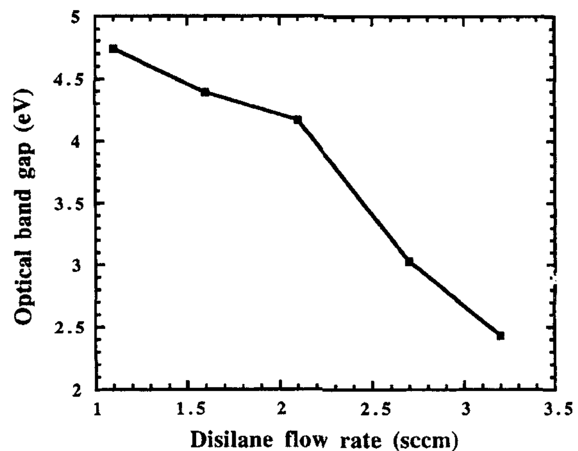

Fig. 2. Variation in optical band gap of silicon nitride films with disilane flow rate

Table 2. Effect of substrate temperature on a-SiN_x:H film properties

Substrate temperature (°C)	Deposition rate (Å min^{-1})	Refractive index	FTIR hydrogen content (%)	ERD hydrogen content (%)	BHF etch rate (Å min^{-1})
370	630.0	2.08	6.0	9.5	25.2
300	585.0	2.04	7.5	13.4	51.7
245	540.0	2.04	14.6	17.7	79.7
350 (PECVD)	56.0	1.88	12.0	—	518.0

and the silicon substrate. This model agreed well with the film composition obtained by XPS sputter depth profiling.

In this section we have shown that various properties of the silicon nitride films can be precisely controlled by adjusting the process parameters. We have obtained high-purity films that can be deposited at high rates with low amounts of hydrogen incorporation. The amount of hydrogen incorporated in such films is significantly lower in comparison with typical plasma-deposited films.

ALUMINIUM NITRIDE

Aluminium nitride (AlN) is a potential dielectric and passivation material for compound semiconductor technology[38,39] and also has been investigated for thermal and optimal applications owing to its good thermal stability, large optical band gap and high thermal conductivity. Growth of aluminium nitride is easily accomplished at high temperatures with either aluminium halides or organometallics.[40,41] Low-temperature growth will be required for applications such as effective passivation of compound semiconductor surfaces in order to avoid preferential sublimation of the more volatile constituent from the semiconductor surface during processing. Aluminium nitride has been grown at low temperatures by sputtering[42] and plasma-enhanced chemical vapour deposition.[43,44] Both of these processes subject the surface to ion bombardment, which can degrade the physical and electrical characteristics of the compound semiconductor surfaces. We have therefore applied by HFCVD approach for the low-temperature deposition of aluminium nitride.[16,27,31]

Trimethylaluminium (TMA) and ammonia were used as reactants. TMA was delivered to the reactor using a conventional bubbler system with helium as the carrier gas. The TMA flow rate was controlled by adjusting the bubbler pressure and the carrier gas flow rate. The bubbler temperature was maintained at 27 °C (300 K) in all experimental runs. TMA tends to be transported as a dimer, so all the flow rates mentioned here will be those for the TMA dimer. The results from several runs have been summarised in Table 3. The filament temperature was held at 1750 °C for all these runs. The film deposition rates were determined by measurement of film thicknesses at 15 points over a 2 inch wafer. The film thickness uniformity was typically ±8%. The aluminium nitride deposition rates and refractive indices were somewhat insensitive to reactor pressure (0.25–4.0 Torr) and substrate temperature (310–460 °C). An experimental run at 4.0 Torr resulted in a low deposition rate and a non-uniform film. The abrupt change in deposition characteristics at 4.0 Torr indicated a possible change in deposition chemistry or controlling mechanism or the formation of a flow recirculation cell over the susceptor. The deposition rates were linearly dependent on the TMA flow rate (in the regime studied here), indicating that the reactor operation was in the reactant transport-limited regime for TMA.

Table 3. Results of aluminium nitride deposition runs. The hydrogen flow rate was set to maintain a total flow rate of 323 sccm. The helium carrier gas flow rate was 30.4 sccm

Film	Substrate temperature (°C)	Reactor pressure (Torr)	Ammonia flow rate (sccm)	TMA dimer flow rate (sccm)	Deposition rate (Å min^{-1})	Refractive index
1	460	0.5	61.9	1.0	1290	1.976
2	375	0.5	61.9	1.0	1160	1.992
3	375	0.5	61.9	1.0	1190	1.989
4	310	0.5	61.9	1.0	1200	1.986
5	375	0.25	61.9	1.0	740	2.000
6	375	1.0	61.9	1.0	1050	1.937
7	375	0.5	61.9	0.4	510	1.944
8	375	0.5	61.9	2.5	2070	2.041
9	375	0.5	30.0	1.0	1150	1.986
10	375	0.5	200.0	1.0	1370	1.959

The atomic composition of the films was determined by X-ray photoelectron spectroscopy (XPS). A typical sputtered depth profile for an aluminium nitride film is shown in Fig. 3. The surface oxide was removed by sputtering to determine the composition of the film bulk. The oxygen and carbon incorporation in the films was strongly dependent on the TMA flow rate. At a low flow rate (0.4 sccm) of TMA about 0.9% carbon and 5% oxygen were detected in the film bulk, whereas at a high flow rate (4.0 sccm) of TMA about 5.8% carbon was detected in the film bulk but no detectable amount of oxygen was seen. The lowest amounts of carbon (0.8%) and oxygen (0.0%) were obtained in a film deposited at 375 °C and TMA flow rate of 1.0 sccm. We also measured the amount of hydrogen incorporated in the films using infrared absorption in the N–H stretching region.[27] The amount of hydrogen incorporated in the films ranged from 2% to 8% on an atomic basis.

The AlN films were specular in appearance. Nomarski inspection of the surface revealed a slight surface texture. The surface morphology and grain structure of the films were studied by scanning electron microscopy. The films were found to have a columnar structure and the column size decreased with increasing substrate temperature. Films up to 1.0 μm thick were deposited under certain conditions without the appearance of stress-induced crackingnoted by others for AlN growth at higher temperatures.[45] Other deposition conditions resulted in films that failed under tensile stress at thicknesses greater than 0.4 μm. In general, high-index films deposited at higher deposition rates would begin cracking at lower film thicknesses (0.3 μm). No measurements of stress in the crack-free films were conducted, however.

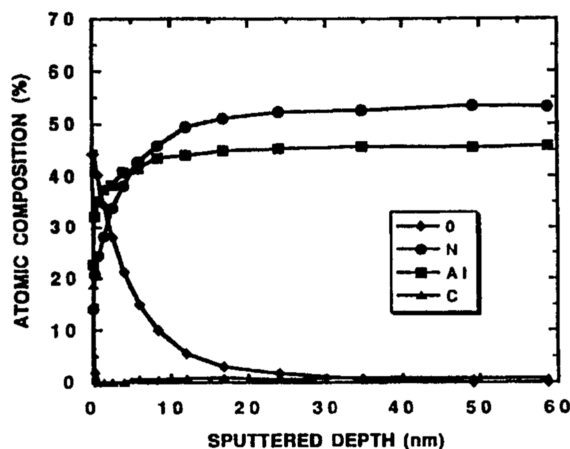

Fig. 3. XPS sputter depth profile of aluminium nitride film 3 deposited at 375 °C and a TMA flow rate of 1.0 sccm

In our experiments on AlN deposition by HFCVD we have shown that high deposition rates in excess of 2000 Å min^{-1} can be achieved at a low substrate temperature of 375 °C. The film deposition rates and compositions are most sensitive to the trimethylaluminium dimer flow rate. Films of high optical density with low levels of oxygen and carbon could be deposited.

TITANIUM NITRIDE

Titanium mononitride (TiN) in thin film form is a good candidate for application in ultralarge-scale integrated (ULSI) circuits as a discussion barrier, an adhesion layer for tungsten deposition and local interconnects.[46,47] Also, owing to its golden colour and high reflectivity for infrared wavelengths, it is a good choice for heat-reflecting and architectural window coatings. It is a refractory nitride (m.p. ≈ 2950 °C) with good thermal and chemical stability, high electrical conductivity, good corrosion and wear resistance and high hardness. In addition, it adheres well to silicon as well as SiO_2 and has very low diffusivities for silicon and metals such as platinum, gold, aluminium and copper. As device geometries shrink to submicron levels and junction depths become shallower, there is an increased need for a barrier layer to avoid junction spiking. Also, with the advent of multilevel metallisation schemes, conformal 'glue' layers (or nucleation layers) are required for interlevel metal deposition and via plug fills.[48] Furthermore, with the drive towards the use of copper as a replacement for aluminium in advanced ULSI circuits, barrier layers will be needed to avoid copper–silicon interdiffusion.[49,50]

We have applied the HFCVD technique for the deposition of TiN films. Titanium tetrachloride ($TiCl_4$) was used as the source of titanium in our studies.[17,32] Titanium chloride was delivered to the reactor by the same bubbler system as described above. The bubbler temperature was maintained at 27 °C in all experimental runs. At 27 °C the vapour pressure of titanium chloride is 12.4 Torr. The titanium source lines were heated to 40 °C in order to avoid any vapour condensation. The gas

dispersal ring was held about 2.0 cm from the susceptor to minimise any complex-forming gas phase reactions between ammonia and titanium chloride. It should be mentioned that under certain deposition conditions there were some particulates observed on the film surface. These surface deposits were water-soluble and did not reappear after a water rinse. These deposits may be complex salts ($TiCl_4 + nNH_3$) formed in the gas phase from $TiCl_4$ and ammonia that are stable below 250 °C, as has been reported elsewhere.[51] The film properties were characterised by various techniques, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, four-point probe, Raman-scattering spectroscopy and Rutherford-backscattering (RBS) measurements.

Table 4 summarises the results from our work on titanium nitride deposition. In the first set of runs (films 1–4) the $TiCl_4$ flow rate was varied by changing the pressure over the source bubbler. The helium carrier gas flow rate was held constant at 30.0 sccm. An increase in $TiCl_4$ flow rate increases the film deposition rate and also increases the oxygen content in the films. As the $TiCl_4$ flow rate is increased, more of the complex-forming gas phase reactions occur[51] and consequently there is a loss of nitrogen-containing precursors. The excess $TiCl_4$ then reacts with the oxygen present in the reactor ambient and forms titanium oxynitride (TiO_xN_y) films. Since TiO_xN_y forms more easily than TiN, the deposition rate increases with increasing $TiCl_4$ flow rate. Furthermore, the colour of the films changes from golden yellow (characteristic of TiN) to red–brown (characteristic of titanium-rich oxynitride films) with increasing titanium chloride flow rate. These results are similar to those reported elsewhere.[52]

In the next set of runs (films 2, 5 and 6) the deposition pressure was varied to study its effect on the film composition. The nitrogen content in the TiN samples could be varied by changing the deposition pressure between 200 and 500 mTorr while keeping all the flow rates constant. All these films were deposited at a temperature of 600 °C. The film stoichiometry changes from titanium-rich (N/Ti = 0.52) at 500 mTorr to nitrogen-rich (N/Ti = 1.2) at 200 mTorr. A decrease in deposition pressure decreases the residence time of the reactant gases in the chamber and therefore decreases the deposition rate. On the other hand, a decrease in reactor pressure increases the lifetime of the nitrogen precursor radicals generated by the hot filament, which consequently increases the nitrogen incorporation in the films. The film resistivity also decreases with decreasing pressure owing to a reduction in oxygen incorporation and deposition of near-stoichiometric films. Films with resistivities as low as 80 μΩ cm were obtained.

Finally, the deposition temperature was changed to study the effect on various film properties (films 6–8). The chlorine and oxygen content, film resistivity, deposition rate and film texture change with increasing deposition temperature from 500 to 600 °C. Fig. 4 shows the effect of increasing substrate temperature on the film microstructure. The film deposited at 600 °C has larger grains than those deposited at lower temperatures, as can be seen from the width of the diffraction peaks. Also, the 600 °C sample has a higher fraction of grains

Table 4. Effect of deposition conditions on TiN film properties

Film	T_{sub} (°C)	P_{dep} (mTorr)	$TiCl_4$ flow (sccm)	Atomic composition (%)				Deposition rate (Å min^{-1})	Resistivity (μΩ cm)
				Ti	N	O	Cl		
1	600	500	0.5	64.3	27.6	6.6	1.1	180.0	273.0
2	600	500	0.75	63.5	32.0	3.5	1.0	170.0	225.0
3	600	500	1.0	63.7	25.8	9.4	1.5	235.0	362.0
4	600	500	2.0	61.2	23.6	14.0	1.3	430.0	340.0
5	600	200	0.75	44.0	52.0	3.5	—	55.0	80.0
6	600	350	0.75	48.0	48.5	3.5	—	107.0	105.0
7	550	350	0.75	45.7	46.0	6.5	1.9	128.0	203.0
8	500	350	0.75	37.0	33.4	22.5	7.0	225.0	870.0

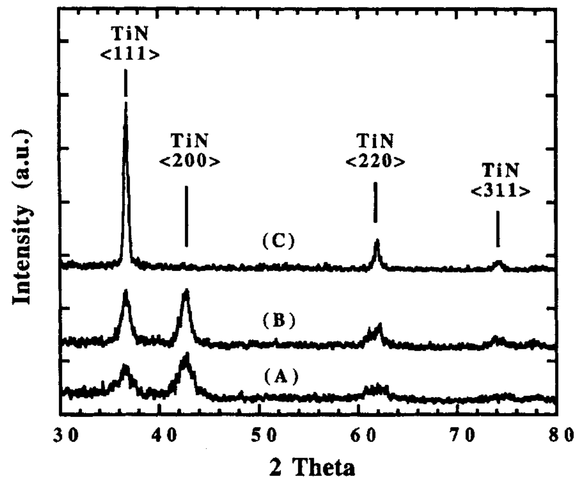

Fig. 4. X-ray diffraction spectra of TiN films deposited at substrate temperatures of (A) 500 °C, (B) 550 °C and (C) 600 °C. All films were deposited at 350 mTorr and a $TiCl_4$ flow rate of 0.75 sccm. The various crystal planes for TiN are indicated

oriented in the ⟨111⟩ direction than the two lower-temperature samples. In addition to increased grain size, the film deposited at 600 °C has a smoother surface than the films deposited at lower temperatures, as shown in Fig. 5.

During routine RBS measurements of film thickness and elemental composition, it was discovered that in some of the films there was a small amount of tungsten at the film–substrate interface. RBS is a sensitive technique to determine metal contamination in films deposited by HFCVD. It has a detection limit of about 10 ppm for heavy metals such as tungsten. Some tungsten was detected at the silicon–titanium nitride interface in films deposited with a 'new' filament, but no tungsten was detected in the bulk of the film. We surmise that this tungsten at the interface is transported to the substrate during the initial start-up of the process from the surface tungsten oxide on the wire (tungsten oxide has a significantly higher

Fig. 5. Scanning electron micrograph of surface of a titanium nitride film deposited at 600 °C

vapour pressure than pure tungsten metal). Furthermore, no tungsten was detected at the interface in subsequent film depositions from the same filament. This observation suggests that for filament temperatures of 1700 °C or below, contamination of the films due to evaporation of tungsten from the hot filament should not be a concern.

In these experiments the problem of low levels of chlorine contamination remains to be solved. In spite of highly reactive nitrogen precursors present in the reactor ambient, low-temperature deposition (<400 °C) was not possible owing to the low reactivity of $TiCl_4$. In summary, we obtained TiN films with resistivities ranging from 80 to 870 μΩ cm, depending on the deposition conditions. The deposition pressure has a significant influence on the film stoichiometry (Ti/N ratio). The substrate temperature has a strong effect on the microstructure. The films obtained at a substrate temperature of 600 °C shows a preferred ⟨111⟩ texture.

DISCUSSION

In studies reported by other groups[12–14] the process gases flowed directly over the hot filament, resulting in a considerable amount of film growth over the filament and the filament assembly. In our approach the use of a bypass gas distribution ring has helped alleviate the problem. Furthermore, we have used higher filament temperatures (>1500 °C), resulting in reduced film deposition on the filament owing to the low sticking coefficient of the depositing material at these high temperatures. The high deposition rates observed in our reactor geometry suggest that there is a considerable amount of activation and/or decomposition of ammonia. The kinetics of ammonia decomposition over various metals have been extensively studied in the literature. It has been shown by laser-induced fluorescence (LIF) that ammonia decomposition over platinum and iron filaments results in production of NH radicals.[37] In this study it was also shown that addition of hydrogen increases the rate of desorption of NH radicals from the surface. In addition to direct decomposition of ammonia, there will be decomposition of molecular hydrogen into atomic hydrogen due to the catalytic action of tungsten. This highly reactive atomic hydrogen can further participate in complex homogeneous gas phase reaction with ammonia and the source gas, producing the necessary precursors for film deposition. Furthermore, besides being a catalytic source of reactive species, the hot filament also provides a hot surface for vibrational activation of reactant molecules and radicals. These vibrationally excited molecules provide an additional source of reactive species.

The chemistry in the HFCVD process consists of complex heterogeneous reactions at the filament surface, followed by homogeneous gas phase reactions and finally heterogeneous reactions on the substrate surface leading to film formation. Our studies have shown that all three steps influence the film properties. The effects of filament temperature, gas composition (and pressure) and substrate temperature have all been addressed in our experiments. This work on hot filament-activated deposition suggests that it is an attractive alternative to conventional methods of material processing. It is a very versatile (and simple) approach for depositing good quality nitride thin films at low temperatures and high rates.

There are a few limitations of this technique at the present time. The application of this method for large-area deposition needs to be explored. The most critical element is the filament design. The filament configuration affects the uniformity of the deposited film and also the uniformity of substrate surface temperature due to radiative heating. The low levels of metal contamination that could occur in the films can become important in determining their electrical properties. Finally, owing to the limited stability of a tungsten filament in an oxidising environment, this technique may not be suitable for deposition of oxygen-containing films.

ACKNOWLEDGEMENTS

This work was supported by grants from the National Science Foundation (CTS-9301386) and Center for Display Technology and Manufacturing at the University of Michigan. The authors also wish to thank Drs. Steve W. Brown and Victor Rotberg for their help with optical characterisation and RBS analysis.

REFERENCES

1. B. V. Spitsyn, L. L. Bouilov and B. V. Derjaguin, *J. Cryst. Growth*, 1981, **52**, 219.
2. S. Matsumoto, Y. Sato, M. Kamo and N. Setaka, *Jpn. J. Appl. Phys.*, 1982, **21**, L183.
3. J. C. Angus and C. C. Hayman, *Science*, 1988, **241**, 913.
4. F. G. Celli and J. E. Butler, *Appl. Phys. Lett.*, 1989, **54**, 1031.
5. W. L. Hsu and D. M. Tung, *Rev. Sci. Instrum.*, 1991, **63**, 4138.
6. S. J. Harris and A. M. Weiner, *J. Appl. Phys.*, 1990, **67**, 6520.
7. E. Kondoh, K. Tanaka and T. Ohta, *J. Appl. Phys.*, 1993, **74**, 4513.
8. S. J. Harris and D. G. Goodwin, *J. Phys. Chem.*, 1993, **97**, 23.
9. D. G. Goodwin, *J. Appl. Phys.*, 1993, **74**, 6888.
10. R. Gat and J. C. Angus, *J. Appl. Phys.*, 1993, **74**, 5981.
11. H. Matsumura, *MRS Symp. Proc.*, 1988, **118**, 43.
12. H. Matsumura, *J. Appl. Phys.*, 1989, **66**, 3614.
13. K. Yasui, H. Katoh, K. Komaki and S. Kaneda, *Appl.Phys. Lett.*, 1990, **56**, 898.
14. R. R. Rye, *J. Vac. Sci. Technol. A*, 1991, **9**, 1099.
15. J. Sumakeris, Z. Sitar, K. S. Ailey-Trent, K. L. More and R. F. Davis, *Thin Solid Films*, 1993, **225**, 244.
16. J. L. Dupuie and E. Gulari, *Appl. Phys. Lett.*, 1991, **59**, 549.
17. S. V. Deshpande and E. Gulari, *MRS Symp. Proc.*, 1994, **327**, 115.
18. H. Wiesmann, A. K. Ghosh, T. McMahon and M. Strongin, *J. Appl. Phys.*, 1979, **50**, 3752.
19. H. Matsumura, *Jpn. J. Appl. Phys.*, 1986, **25**, L949.
20. J. Doyle, R. Robertson, G. H. Lin, M. Z. He and A. Gallagher, *J. Appl. Phys.*, 1988, **64**, 3215.
21. A. H. Mahan, J. Carapella, B. P. Nelson, R. S. Crandall and I. Balberg, *J. Appl. Phys.*, 1991, **69**, 6728.
22. P. Brogueira, S. Grebner, F. Wang, R. Schwarz, V. Chu and J. P. Conde, *MRS Symp. Proc.*, 1993, **297**, 121.
23. S. V. Deshpande, J. L. Dupuie and E. Gulari, *Appl. Phys. Lett.*, 1992, **61**, 1420.
24. J. L. Dupuie, E. Gulari and F. L. Terry, *J. Electrochem. Soc.*, 1992, **139**, 1151.
25. S. V. Deshpande, E. Gulari, S. W. Brown and S. C. Rand, *MRS Symp. Proc.*, 1994, **325**, 177.
26. S. V. Deshpande, E. Gulari, S. W. Brown and S. C. Rand, *J. Appl. Phys.*, 1995, **77**, 6534.
27. J. L. Dupuie and E. Gulari, *J. Vac. Sci. Technol. A*, 1992, **10**, 18.
28. S. V. Deshpande, E. Gulari, S. J. Harris and A. M. Weiner, *Appl. Phys. Lett.*, 1994, **65**, 1757.
29. S. Yu, S. V. Deshpande, E. Gulari and J. Kanicki, *MRS Symp. Proc.*, 1995, **377**, in press.
30. J. L. Dupuie and E. Gulari, *J. Appl. Phys.*, 1992, **71**, 4030.
31. J. L. Dupuie, *Ph.D. Thesis*, University of Michigan, Ann Arbor, MI, 1991.
32. S. V. Deshpande, *Ph.D. Thesis*, University of Michigan, Ann Arbor, MI, 1994.
33. K. E. Bean, P. S. Gleim and R. L. Yeakley, *J. Electrochem. Soc.*, 1967, **114**, 733.
34. A. J. Lowe, M. J. Powell and S. R. Elliot, *J. Appl. Phys.*, 1986, **59**, 1251.
35. A. Piccirillo and A. L. Gobbi, *J. Electrochem. Soc.*, 1990, **137**, 3910.
36. W. A. Lanford and M. J. Rand, *J. Appl. Phys.*, 1978, **49**, 2473.
37. G. S. Selwyn and M. C. Lin, *Chem. Phys.*, 1982, **67**, 213.
38. S. Fujieda, M. Mizuta and Y. Matsumoto, *Jpn. J. Appl. Phys.*, 1988, **27**, L296.
39. Y. Mochizuki, M. Mizuta, S. Fujieda and Y.Matsumoto, *Appl. Phys. Lett.*, 1989, **55**, 1318.
40. Y. G. Roman and A. P. M. Adriaansen, *Thin Solid Films*, 1989, **169**, 241.
41. H. Kawakami, K. Sakurai, K. Tsubouchi and N. Mikoshiba, *Jpn. J. Appl. Phys.*, 1988, **27**, L161.
42. F. S. Ohuchi and P. E. Russel, *J. Vac. Sci. Technol. A*, 1987, **5**, 1630.
43. M. David, S. V. Tabu and D. H. Rasmussen, *AIChE J.*, 1990, **36**, 871.
44. F. Hasegawa, T. Takahashi, K. Kubo, S. Ohnari, Y. Nannichi and T. Arai, *Jpn. J. Appl. Phys.*, 1987, **26**, L1448.
45. H. M. Manasevit, F. M. Erdmann and W. I. Simpson, *J. Electrochem. Soc.*, 1971, **118**. 1864.
46. M.-A. Nicolet, *Thin Solid Films*, 1978, **52**, 415.
47. J. R. Lineback, *Electronics*, 1987, 23 July, p. 63.
48. Y. Nakasaki, K. Suguro, S. Shima and M. Kashiwagi, *J. Appl. Phys.*, 1988, **64**, 3263.
49. T. E. Siedel, *MRS Symp. Proc.*, 1992, **260**, 3.
50. J. O. Olowolafe, J. Li and J. W. Mayer, *J. Appl. Phys.*, 1990, **68**, 6207.
51. S. R. Kurtz and R. G. Gordan, *Thin Solid Films*, 1986, **140**, 277.
52. M. J. Buiting and A. F. Otterloo, *J. Electrochem. Soc.*, 1992, **139**, 2580.

BIOGRAPHIES

Dr. Sadanand V. Deshpande received his B.Tech. in Chemical Engineering in 1988 from the Indian Institute of Technology, Kanpur, India. He then did his M.S. in Chemical Engineering from Illinois Institute of Technology, Chicago in 1990. Thereafter, Dr. Deshpande decided to work towards his Ph.D. in the area of Chemical Vapor Deposition of Nitride and Carbide thin

films. In 1994, he finished his doctoral work under Professor Erdogan Gulari at the University of Michigan, Ann Arbor. Dr. Deshpande is currently a Postdoctoral Research Fellow at the Center for Display Technology and Manufacturing, University of Michigan. His research interests include studying alignment layers for liquid crystal displays, and particle and radical species detection in plasma chemical vapor deposition systems.

Dr. Jeffrey L. Dupuie received his B.S. degree in Chemical Engineering from Wayne State University in 1986. He subsequently was awarded a National Science Foundation Fellowship which he used to study thin film deposition and materials characterization under Professor Erdogan Gulari at the University of Michigan. He received his Ph.D. in Chemical Engineering in 1991. Following a short-term research fellowship, in which he continued his research in filament activated chemical vapor deposition, he joined Motorola's Advanced Product Research and Development Laboratory in 1992. Then in 1994, Dr. Dupuie joined Ford Motor Company, Automotive Components Division, where he has worked on assessment of paint durability and plasma treatment of plastics. He is currently investigating the use of Time of Flight Secondary Ion Mass Spectroscopy (TOFSIMS) as a tool for characterizing the durability of paints on plastic, and the development of improved approaches for predicting the performance of plastic materials systems.

Professor Erdogan Gulari received his B.S. in Chemical Engineering from Roberts College, Istanbul, Turkey in 1969. He obtained his Ph.D., working with Professor Cornelius J. Pings, at the California Institute of Technology in 1973. After a short stint of industrial work in Turkey, he came back to the United States in 1976 to do Postdoctoral work with Professor Benjamin Chu of SUNY at Stony Brook, and has been on the faculty of the University of Michigan, College of Engineering, since 1978. His research interests are in the areas of catalysis, adsorption and thin film growth.