Japanese Journal of Applied Physics
Vol. 43, No. 4A, 2004, pp. 1619–1624

# Improvement of TiN Flow Modulation Chemical Vapor Deposition from $TiCl_4$ and $NH_3$ by Introducing Ar Purge Time

Keeyoung JUN, Ik-Tae IM[1] and Yukihiro SHIMOGAKI*

*Department of Materials Engineering, School of Engineering, Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[1]*Dept. of Automotive Engineering, Iksan National College, 194-5 Ma-dong, Iksan 570-752, Korea*

(Received December 2, 2003; accepted January 22, 2004; published April 9, 2004)

TiN films were deposited by using $TiCl_4/NH_3$ flow modulation chemical vapor deposition (FMCVD). FMCVD consists of repetitive TiN deposition periods by $TiCl_4/NH_3$, each of which is followed by Cl reduction period. TiN deposition periods are typically 3 s and Cl reduction periods are 1 s. The effect of the number of deposition/reduction cycles and the effect of the partial pressure of $TiCl_4$ and $NH_3$ on film uniformity and resistivity were investigated. For a total reduction period of 100 s, increasing the number of reduction periods from 100 × 1-s periods to 300 × 0.33-s periods decreased the step coverage. This decrease in coverage was due to residual $TiCl_4$ during the Cl reduction period by $NH_3$ that cleared out $TiCl_4$ at a constant rate, independent of the length of the period of reduction cycle. An Ar purge cycle was used between the deposition and reduction cycles to allow the residual $TiCl_4$ to clear out before the $NH_3$ was used for the film reduction cycle. This significantly improved the film step coverage from 50% to over 90%. The minimum film resistivity occurred when the $NH_3$ partial pressure was 0.25 Torr. $NH_3$ partial pressure less than 0.25 Torr inhibited film reduction, and $NH_3$ partial pressure higher than 0.25 Torr enhanced the deposition rate, which also inhibited film reduction. By using the optimum conditions determined in this study, we could obtain TiN films that had film resistivity of about 240 μΩ·cm and step coverage of about 98% at 410°C.
[DOI: 10.1143/JJAP.43.1619]

KEYWORDS: flow modulation chemical vapor deposition (FMCVD), titanium nitride (TiN), $TiCl_4$, $NH_3$, process optimization, Ar purge, partial pressure, step coveerage, resistivity

## 1. Introduction

Titanium nitride (TiN) has been widely investigated because of its many applications, such as wear-resistant coating on tools,[1,2] activated surfaces for copper seed layers grown by electrolysis plating,[3] and TiN also used as a diffusion barrier layer for ultra-large-scale integrated circuit (ULSI) applications. Diffusion barriers, however, must have good step coverage to achieve uniformity, must prevent diffusion of metals, must be chemically inert, and must have low resistivity when used in multi-level metallization applications.[4–6] TiN is most commonly deposited by sputtering, often from a titanium target in a nitrogen-containing atmosphere.[7–9] Sputtered films can be produced by controlling the stoichiometry and crystal orientations, thus yielding film resistivities as low as 20–40 μΩ·cm. However, uniform deposition over high-aspect-ratio holes and trenches is difficult to achieve. Sputtered barrier layers are particularly thin at the bottom corners of via holes, and failure of the film can occur at such locations.[10,11]

Chemical vapor deposition (CVD) can provide uniform step coverage over high-aspect-ratio features. CVD can be used to deposit TiN films from either $TiCl_4/NH_3$-based chemistry,[12,13] or from metal organic precursors such as tetrakis-dimethyl-amido-titanium (TDMAT)[14–16] and tetrakis-diethyl-amido-titanium (TDEAT).[17,18] TiN films deposited using $TiCl_4/NH_3$ CVD have excellent step coverage and acceptable electrical properties for ULSI metal-barrier applications.[19,20] The process temperature should be higher than 600°C to realize low resistivity and impurities. However, deposition temperatures lower than 450°C are required for TiN-CVD in multilayer metallization applications, such as via metallization. Hegde *et al.*[21] reported that TiN films deposited using $TiCl_4/NH_3$ at low temperature, between 400 and 550°C, contained large amounts of chlorine and oxygen impurities. Cl is a major impurity of TiN films from $TiCl_4$-based chemistry, and the film resistivity is proportional to the Cl concentration.[22] In contrast, TiN films deposited at high temperature, 700°C, contained as little as 1 at.% of Cl and no O. Post-deposition annealing[23,24] and $NH_3$ plasma treatment[25] have been used to decrease the resistivity and to remove Cl from TiN films.

The introduction of organic reactants, such as TDMAT and TDEAT, was proposed for low-temperature deposition suitable for ULSI multi-level metallization processes.[14–18] However, TiN films deposited from organic reactants had many impurities, such as carbon and oxygen, yielding films with high resistivity.[26] Thus, additional post treatments such as plasma treatment were also required for these films.[27,28]

Atomic layer deposition (ALD)[29–32] has been used to deposit TiN films at 450°C, with Cl concentrations less than 0.5 at.%. The advantages of ALD over CVD and physical vapor deposition (PVD) processes are low resistivity of the deposited films (120 μΩ·cm) and high step coverage (near 100%). However, ALD requires long processing times and Ar purging for each cycle to achieve uniform films. Therefore, the throughput is low and a relatively large quantity of source gas is used, making it unacceptable for commercial applications.

Hamamura *et al.*[33,34] developed a flow modulation chemical vapor deposition (FMCVD) method for reducing residual Cl in TiN films. TiN-FMCVD consists of alternating TiN film deposition and Cl reduction by $NH_3$. TiN films formed with FMCVD have a relatively low resistivity of about 250 μΩ·cm at relatively low deposition temperatures of 380°C, and have good step coverage over 90%. These results were obtained by optimizing the flow modulation sequences. The other deposition parameters, such as partial pressures of $TiCl_4/NH_3$ and deposition temperature were fixed in their work at 0.02 Torr/0.5 Torr and 380°C, respectively.

In this work, we studied the effect of the deposition

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*E-mail address: shimo@dpe.mm.t.u-tokyo.ac.jp

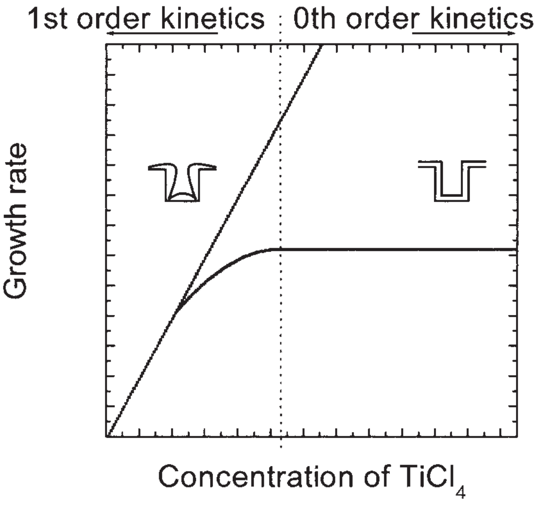

Fig. 1. Langmuir–Hinshelwood reaction mechanism.

temperature and the partial pressure of $TiCl_4$ and $NH_3$ on TiN films for the further improvement on the FMCVD developed by Hamamura *et al.* We introduced Ar purge period between the TiN deposition period and Cl reduction period to realize lower resistivity of 240 μΩ·cm without degrading step coverage, although $NH_3$ reduction time was shorter from 200 s to 100 s in total process time.

## 2. Basic concept of FMCVD

FMCVD is one of the advanced CVD processes for future ULSI devices. The basic concept of FMCVD is to introduce cyclic operation into normal CVD to enhance surface adsorption/desorption of reacting species, to control the nucleation on growing surfaces, to introduce multi-step deposition and reduction cycles for better film properties.

Generally, the reaction mechanism governing the surface deposition and reaction of $TiCl_4$ is known as the Langmuir–Hinshelwood mechanism, and is shown in Fig. 1. Langmuir–Hinshelwood isotherms are given for the adsorption of $TiCl_4$ and the reaction rate, $r$, is expressed as

$$r = \frac{k_r K C_{sTi}}{1 + rKC_{sTi}}, \tag{1}$$

where, $k_r$, $K$, and $C_{sTi}$ are the surface reaction rate constant of adsored species, equilibrium constant of adsorption, and the concentration of Ti containing species, respectively. For $KC_{sTi} \gg 1$, the reaction becomes 0th-order (i.e., $r = k_r$), because the adsorption sites are almost completely covered by adsorbates. The 0th-order reaction is favorable for uniform step coverage due to its nearly constant deposition rate for different source concentrations. For $KC_{sTi} \ll 1$, the reaction becomes first-order with $TiCl_4$ concentration (i.e., $r = k_r KC_{sTi}$), because of the adsorption sites are unoccupied. 1st-order reaction may result in poor step coverage due to its growth rate sensitivity against source concentration. To realize 0th-order reactions for an excellent step coverage quality, the $P_{TiCl_4}$ must be higher than 0.01 Torr.[35] But the high $TiCl_4$ concentrations required for the 0th-order reaction increases the Cl concentration in the films. We therefore used a reduction cycle to reduce the film Cl concentration. Figure 2 shows the FMCVD sequence of alternate TiN film deposition using $TiCl_4/NH_3$ and Cl reduction using $NH_3$.

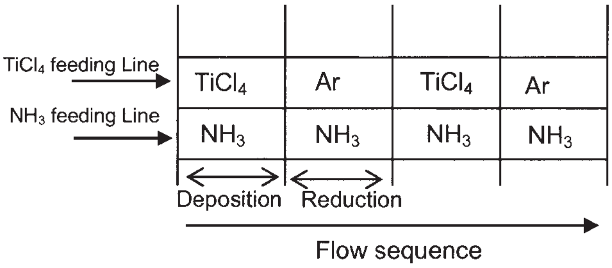

Fig. 2. FMCVD sequence consisting of alternate deposition and reduction periods.

The essential advantage of FMCVD over the post annealing process is the time constant required for reducing the chlorine in the film. As the Cl reduction is controlled by diffusion of the reduction agent or Cl containing species through the film, the reduction time $\tau$, that is required for post treatment onto the TiN film deposited by normal CVD, can be given as

$$\tau \propto \frac{L^2}{D}, \tag{2}$$

where $L$ is the diffusion length corresponding to the film thickness, and $D$ is the diffusion coefficient of the reduction gas or chlorine containing species in the deposited film. We deposit TiN film by FMCVD using $N$ times cycle, the film thickness in one cycle is $1/N$ of normal CVD. The number of cycles, which includes the deposition period and the reduction period, is determined FM-number, $N$. Then, Cl reduction time in FMCVD, $\tau'$ can be given as

$$\tau' \propto \frac{\left[\frac{L}{N}\right]^2}{D} \times N, \tag{3}$$

and we can obtain the following equation expressed as

$$\tau' = \frac{\tau}{N}. \tag{4}$$

Equation 4 shows that the increase of $N$ is expected to decrease the film Cl concentration, because the time required to remove residual Cl, $\tau'$, will be decreased. Thus, the increase of FM number, $N$ resulted to achieve the low resistivity at low deposition temperature.

## 3. Experiment

Figure 3 shows a schematic of the FMCVD reactor. $TiCl_4$ was introduced by using a bubbling system with Ar as the carrier gas. The bubbler was immersed in a thermobath maintained at 60°C. The gas flow sequencing was computer controlled, and a three-way valve was used to sequentially switch feeding gases. $TiCl_4$ and $NH_3$ were introduced into the reactor through separate feed lines to prevent premature product formation. A warm-wall reactor was used to prevent deposition of $TiCl_4$ and $NH_3$ onto the reactor wall. The wall temperature was maintained at 180°C, and the substrate heater temperature was set to 650°C to maintain a substrate temperature ($T_{sub}$) of 410°C.

The total process time ($\tau_{total}$) was maintained at 400 s (300 s for deposition and 100 s for reduction). The FM number ($N$), was 100, 150, and 300, where FM-100 was 100 cycles of 3-s deposition and 1-s reduction, FM-150 was 150

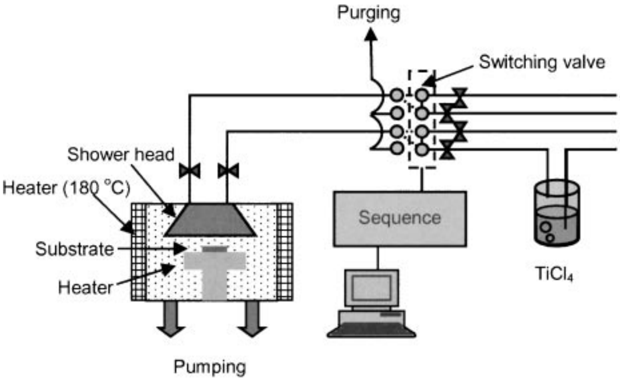

Fig. 3. Schematic of the FMCVD reactor.

cycles of 2-s deposition and 0.67-s reduction, and FM-300 was 300 cycles of 1-s deposition and 0.33-s reduction.

TiN films were deposited on silicon wafers covered with 100-nm thermal oxide films, and the step coverage was estimated by depositing films on silicon substrates with trench structures with an aspect ratio of 5 : 1. The total pressure was 2 Torr, and the partial pressure of $TiCl_4$ ($P_{TiCl_4}$) ranged from 0.01–0.02 Torr and that of $NH_3$ ($P_{NH_3}$) from 0.25–1.0 Torr. The total flow rate of $TiCl_4$ (carried by Ar), $NH_3$, and Ar as diluent gas was 355 sccm. The thickness of the films was measured by using field emission scanning electron microscopy (FE-SEM, JEOL 6340F) and the sheet resistivity was measured by using a 4-point probe method. X-ray photoelectron spectroscopy (XPS, ULVAC-$\phi$ 1600C) was used to determine the atomic ratios of Ti, N, and Cl in the TiN films.

## 4. Results and Discussion

Figure 4 shows the relationship between the deposition temperature ($T_{sub}$), film resistivity, and film Cl concentration for FM-100 sequencing conditions. The film resistivity and Cl content decreased with increasing $T_{sub}$. However, because the deposition temperature must be maintained at less than 450°C for multi-level metallization, our experiments were done at $T_{sub} = 410$°C.

Experiments were done for $N = 100$, 150, and 300 and for $P_{TiCl_4}$ of 0.01 and 0.02 Torr. Figure 5 shows the film resistivity as a function of $N$ and $P_{TiCl_4}$. The resistivity decreased with increasing $N$ and with decreasing $P_{TiCl_4}$. The deceased film resistivity mainly derived from Cl reduction. The lowest film resistivity was obtained for $N = 300$ and for $P_{TiCl_4}$ of 0.01 Torr. Increasing of FM-number ($N$) to 300 from 100 resulted in lowering the film resistivity by 20%, however, the amount of Cl reduction is not so much as expected from eqs. (2)–(4). This may be due to the residual $TiCl_4$ during Cl reduction period, which is discussed later.

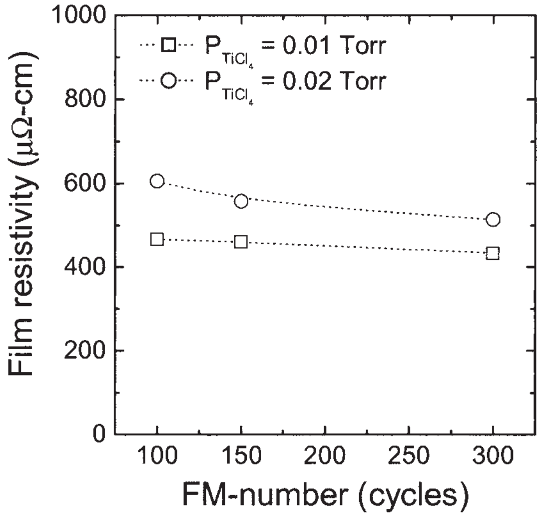

Fig. 5. Resistivity of FMCVD TiN films as a function of FM number and $TiCl_4$ partial pressure.

Figure 6 shows the step coverage as a function of $N$. Experiments were done for operating conditions yielding step coverage of about 90% in normal CVD processes. Good step coverage over 90% was obtained for $N = 100$, independent of $P_{TiCl_4}$. However, the step coverage decreased with increasing $N$ or with decreasing $P_{TiCl_4}$. When $N = 300$, the step coverage decreased to about 50%.

Figure 7 shows time-dependent concentration profile of $TiCl_4$ and $NH_3$ in the reactor. The solid lines show the intended profiles and the dotted lines show the actual

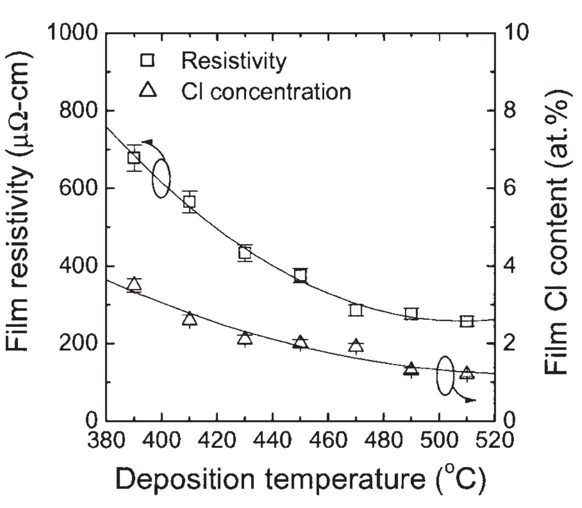

Fig. 4. Film resistivity and Cl content as a function of deposition temperature.

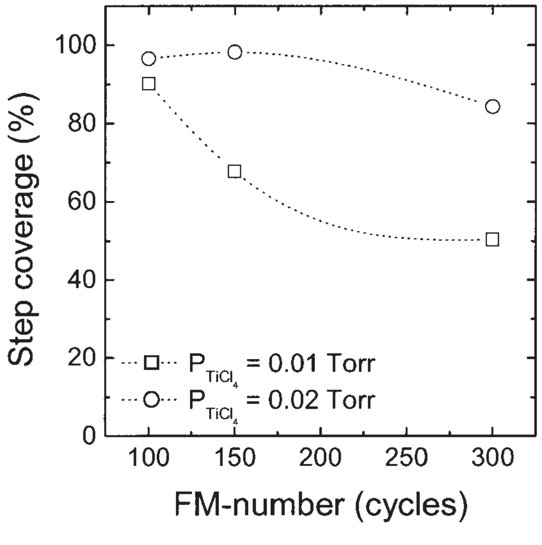

Fig. 6. Step coverage of FMCVD TiN films as a function of FM number, $N$.

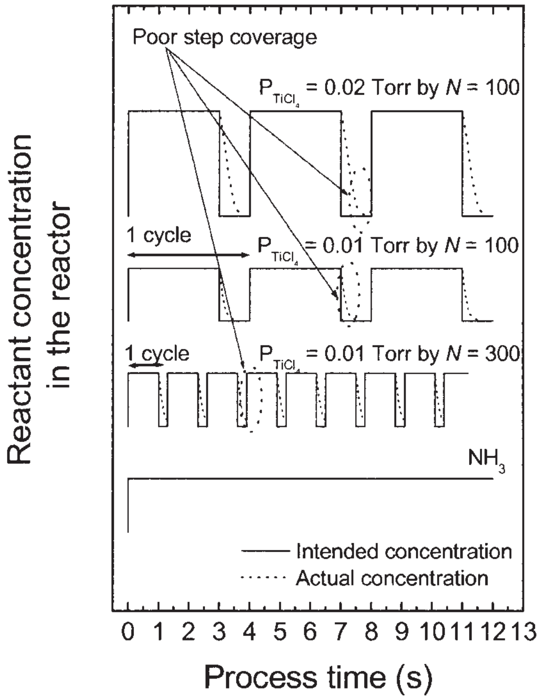

Fig. 7. $TiCl_4$ intended and actual time-dependent concentration.

profiles. During the reduction period, the intent is to instantaneously decrease the $TiCl_4$ concentration to 0. However, as shown in Fig. 7, the $TiCl_4$ concentration in the chamber decreases to 0 over a finite time period. The $TiCl_4$ reactant that remains in the chamber during the reduction period reacts with the $NH_3$, at progressively lower $TiCl_4$ partial pressures. According to the behavior shown in Fig. 1, as the $TiCl_4$ partial pressure approaches 0, the reaction becomes first-order, creating non-uniform films. Because the decrease to 0 $TiCl_4$ concentration occurs over a finite time, which is independent of $N$, for a given total deposition time period, increasing $N$ implies that the total fraction of time for which first-order reactions are active increases, and therefore the overall film uniformity decreases. However, if the $TiCl_4$ partial pressure during film growth is 0.02 Torr, the $TiCl_4$ concentration during Cl reduction by $NH_3$ might be sufficiently high to minimize the time during which first-order reactions are active, and thereby achieve better step coverage than for film growth at $P_{TiCl_4}$ of 0.01 Torr.

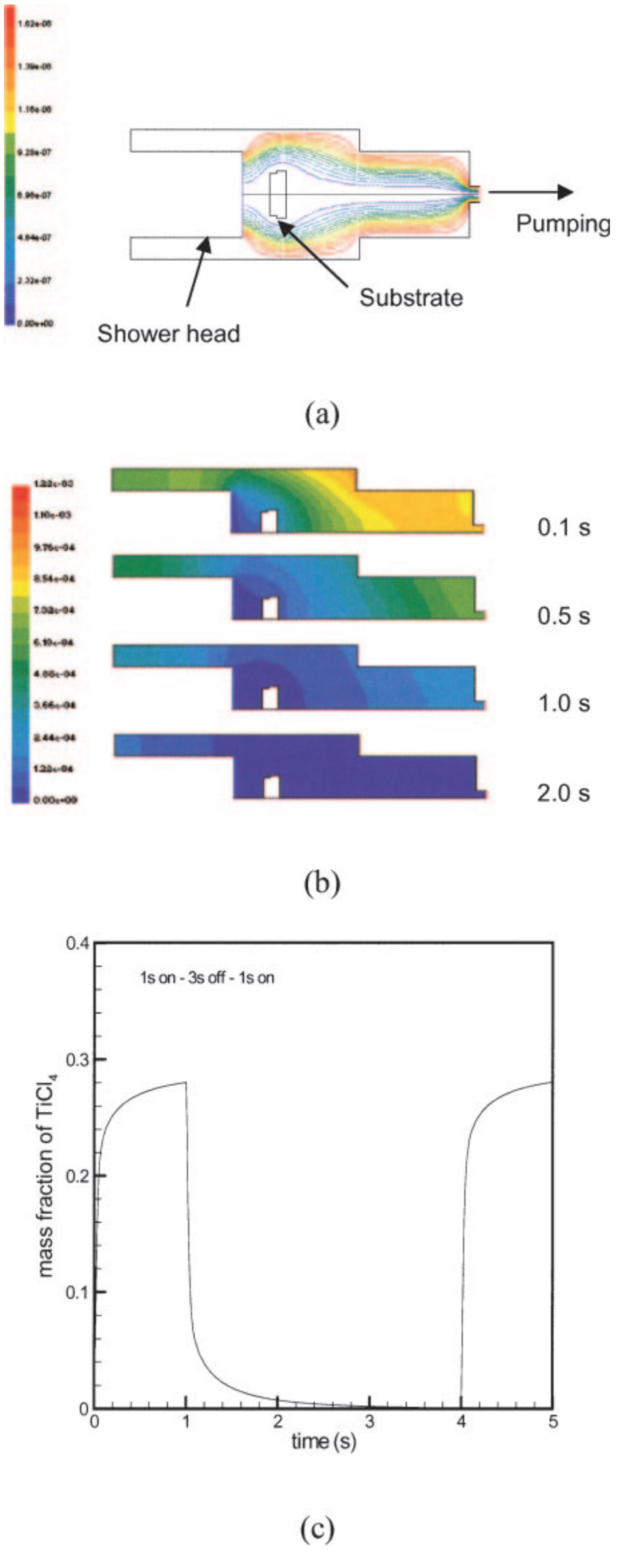

Fig. 8. FLUENT-simulated time-dependent $TiCl_4$ concentration in the reactor after $TiCl_4$ flow is shut off: (a) steady-state stream function, (b) $TiCl_4$ concentration during the $NH_3$ reduction period 0.1, 0.5, 1.0, and 2.0 s after $TiCl_4$ flow is shut off, (c) mass fraction of $TiCl_4$ on the substrate for 1.0 s-supply, 3.0 s-reduction, and 1.0 s-supply.

Because of the effect of $TiCl_4$ on the uniformity of the film formation during the reduction cycle, we used the computational fluid dynamics (CFD) program FLUENT 5.5[36)] to simulate the time-dependent $TiCl_4$ concentration in the reactor. The simulated processes included convection and diffusion of $TiCl_4$ in the chamber. Surface reactions were not considered. We investigated the residual $TiCl_4$ in the chamber after the switching $TiCl_4$/Ar gas flow to pure Ar flow in $TiCl_4$ feeding line. Figure 8 shows the simulation results and Fig. 8(a) shows the steady-state stream function. Figure 8(b) shows $TiCl_4$ concentration contours as a function of time after the $TiCl_4$ flow is shut off. We can know the surface concentration of $TiCl_4$ on the substrate from these calculations. Figure 8(c) shows the mass fraction of $TiCl_4$ on the substrate as a function of time after the $TiCl_4$ flow is shut off. $TiCl_4$ is on for 1 s, then $NH_3$ is on for 3 s, then $TiCl_4$ is on for 1 s for this calculation. Figure 8 indicates that a little amount of $TiCl_4$ remains 0–0.3 s after the $TiCl_4$ flow is shut off, and that the $TiCl_4$ concentration significantly decreases after 1 s. The deposition of TiN film by these remaining $TiCl_4$ with $NH_3$ will cause poor step coverage due to the low concentration. Therefore, TiN films formed at $N = 300$ had

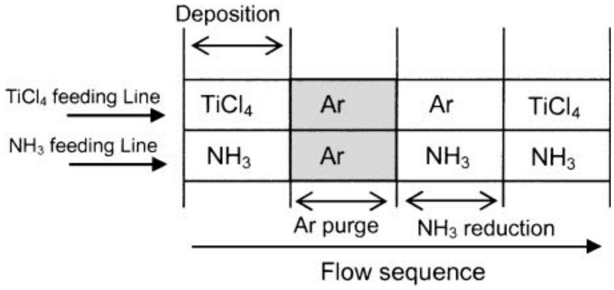

Fig. 9. Modified FMCVD sequence consisting of deposition, Ar purge, and reduction periods.

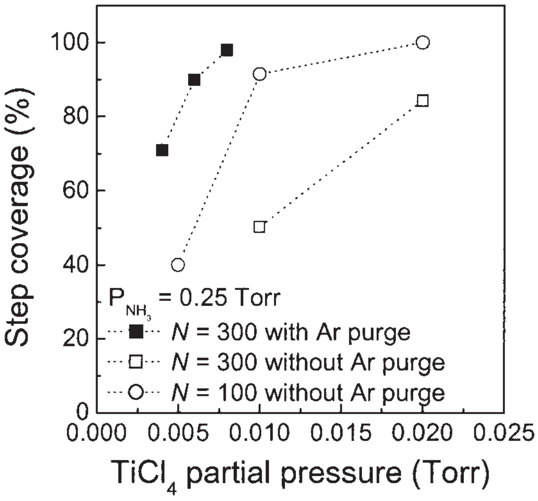

Fig. 10. Step coverage of films deposited using FMCVD with an Ar purge period.

poorer step coverage than did those at $N = 100$, because there were 3 times more reduction cycles over which non-conformal deposition occurred.

To minimize the formation of non-uniform films, we added an Ar-purge period between the deposition and reduction periods, to remove the remaining $TiCl_4$ before $NH_3$ was added for the reduction reactions. Figure 9 shows the modified FMCVD sequence with the additional Ar purge period. According to the simulation, Ar purge period of 1 s may be enough to clear out $TiCl_4$ from the reactor. Figure 10 shows the step coverage at various $P_{TiCl_4}$ by the original sequence and the modified sequence with Ar purge period of 1 s. The step coverage at $P_{TiCl_4} \cong 0.01$ Torr was improved from 50 to 98% when $N = 300$. We could deposit TiN films with better step coverage by the modified sequence than original process with $N = 100$. That means lower resistivity and better step coverage can be obtained by introducing the Ar purge period. Figure 11 shows the film resistivity vs. $P_{TiCl_4}$, and indicates that the resistivity of the films fabricated with FMCVD with the Ar purge cycle was about half that without the Ar purge cycle. The films formed with the Ar purge period therefore have step coverage of about 98% and resistivity of about 240 $\mu\Omega$·cm.

The effect of the partial pressure of $NH_3$ on the film properties was also investigated. Figure 12 shows the film growth rate as a function of $P_{NH_3}$. The growth rate was proportional to $P_{NH_3}$ from 0.1 to 1.0 Torr. The growth rate of TiN films increased with $P_{NH_3}$ according to the Eley-Rideal reaction mechanism.[35)]

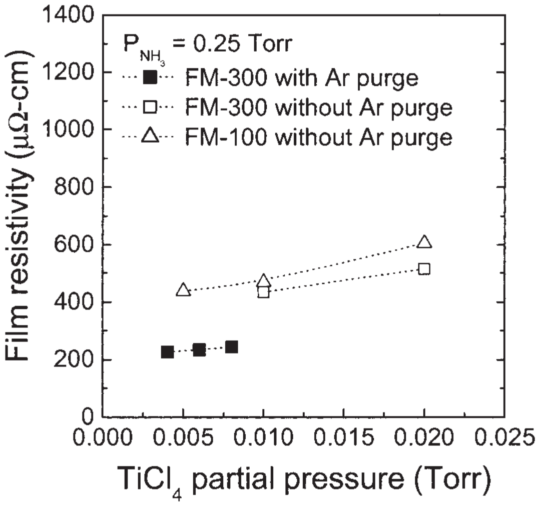

Fig. 11. Resistivity of films deposited using FMCVD with an Ar purge period.

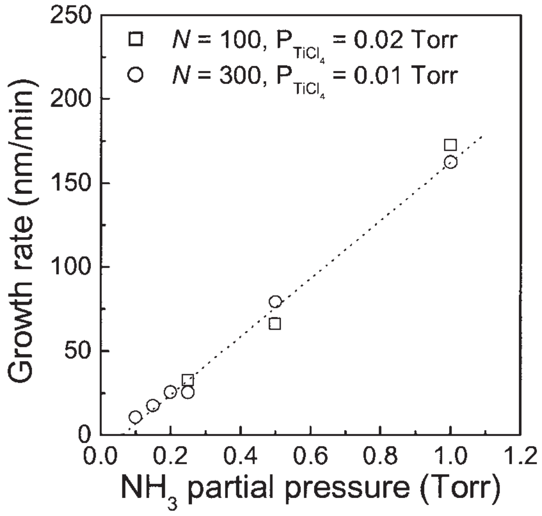

Fig. 12. Growth rate as a function of $NH_3$ partial pressure.

Figure 13 shows the measured film resistivity as a function of $P_{NH_3}$, and indicates that the film resistivity was a minimum for $P_{NH_3}$ of 0.25 Torr and increased for either lower or higher $NH_3$ partial pressure. The reason is that at lower $NH_3$ partial pressures the Cl reduction decreases, and at higher $NH_3$ partial pressures Cl desorption rates decrease due to thicker films deposited during the deposition cycle. Therefore, a minimum film resistivity occurs.

## 5. Conclusions

TiN films were deposited by using $TiCl_4/NH_3$ flow modulation chemical vapor deposition (FMCVD),where alternating growth and reduction cycles were used to deposit films with low chlorine content. The effect of $TiCl_4$ and $NH_3$ partial pressures on the TiN film uniformity and resistivity was studied. Increasing FM-number ($N$) to 300 from 100 resulted in lowering the film resistivity by 20%, and step coverage quality became poor when $P_{TiCl_4} = 0.01$ Torr. $TiCl_4$ remaining in the reactor during the reduction cycle

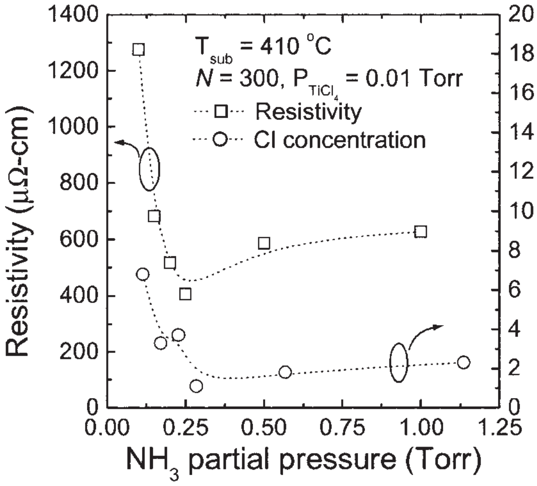

Fig. 13. Resistivity as a function of $NH_3$ partial pressure.

prevented effective Cl reduction and, also caused poor film step coverage. An Ar purge period was introduced to improve the step coverage. With the Ar purge cycle, the fabricated films had step coverage of about 98% and resistivity of about 240 μΩ·cm. An $NH_3$ partial pressure of about 0.25 Torr yielded the lowest film resistivity. The FMCVD allowed control of the TiN film growth rate, step coverage, resistivity, and Cl concentration by varying the partial pressure of the reactants. By using the optimum conditions ($P_{TiCl_4} = 0.008$ Torr, $P_{NH_3} = 0.25$ Torr, $N = 300$, and Ar purge time = 1 s/cycle) determined in this study, we used FMCVD at a temperature of 410°C to deposit TiN films that had film resistivity of about 240 μΩ·cm and step coverage of about 98%. The total through put under this condition was 5 nm/min, which is nearly 10 times faster than ALD processes.

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