

TiN Films Prepared by Flow Modulation Chemical Vapor Deposition using TiCl_4 and NH_3

HirotaKa HAMAMURA, Hiroshi KOMIYAMA and Yukihiro SHIMOGAKI¹

Department of Chemical System Engineering, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

¹*Department of Metallurgy and Material Sciences, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

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We propose a new chemical vapor deposition (CVD) process, the flow modulation chemical vapor deposition (FMCVD) process, to obtain high quality titanium nitride (TiN) films at low deposition temperature in a single CVD chamber. FMCVD uses sequential deposition and reduction processes, such as the deposition of TiN films followed by chlorine reduction. This cycle was repeated to achieve sufficient film thickness. By decreasing the thickness in one cycle, the residual chlorine concentration and the resistivity of the films decreased. Using FMCVD process, we could achieve low resistivity ($250\ \mu\Omega\text{cm}$), low residual chlorine concentration (2 at.%) with uniform step coverage at low deposition temperature (380°C).

KEYWORDS: chemical vapor deposition, titanium nitride, flow modulation, resistivity, chlorine reduction

1. Introduction

There are many demands in chemical vapor deposition (CVD) processes for the fabrication of advanced ULSI devices. As ULSI feature sizes have shrunk to sub micron dimensions, we have to control the stoichiometry, crystal orientation, grain size and micro roughness of nanometer scale thin films. Additionally we have to control the interface structure between the initial surface and the deposited films. These precise controls of film structures require advanced operating concepts for the CVD process. The conventional CVD process uses fixed operating conditions, like temperature, total pressure, precursor concentration, and gas flow rate, but these operating parameters should be dynamically changed to obtain tailor-made film structures.

TiN has been widely used as a diffusion barrier layer in ULSI process because of its high thermal stability, good diffusion barrier properties, and low electrical resistivity. TiN is primarily used as a barrier layer to prevent interdiffusion of Si and Al metallization, and as an adhesive and nucleation layer for blanket tungsten CVD. Conventionally, TiN films are deposited by physical vapor deposition (PVD) using reactive sputtering. As ULSI feature sizes have shrunk to sub micron dimensions, the ability of a physical technique to deposit films uniformly has become of concern. The poor step coverage of sputtered films, especially in sub micron contact holes with high aspect ratios, has been shown to lead barrier property degradation and adhesion loss.¹⁾ Therefore, conformal processes for the deposition of TiN films are required for the fabrication of advanced ULSI devices. CVD processes offer the potential advantage of good step coverage.

Two types of CVD processes are used currently: one based on inorganic precursors, such as $\text{TiCl}_4/\text{NH}_3$, and the other based on metallorganic precursors, such as tetrakis(dimethylamino)-titanium (TDMAT)²⁾ and tetrakis(diethylamino)-titanium (TDEAT).³⁾ Using these metallorganic CVD processes, it is possible to deposit TiN films at low deposition temperature ($300\text{--}400^\circ\text{C}$), but the high residual carbon impurity concentration and porous structure of the films are the major drawbacks of this process.⁴⁾ TiCl_4 -based CVD processes usually provide low resistivity, good diffusion barrier properties and excellent step coverage. Nevertheless, this specific process cannot be applied to upper metallization process, because it requires high deposition

temperature (above 600°C) to obtain low resistivity and low residual chlorine concentration with good step coverage.^{5–10)} At low deposition temperature (below 400°C), the high partial pressure of TiCl_4 produces excellent step coverage, but the films contain high residual chlorine and the resistivity of the films is high; on the other hand, low partial pressure of TiCl_4 produces low residual chlorine and low resistivity, but the films have poor step coverage. To decrease the residues of TiN films using the high TiCl_4 concentration process, post deposition annealing^{11,12)} and plasma treatment¹³⁾ are used, but these processes require additional reactors and time.

Recently, an atomic layer deposition (ALD) method has been proposed to deposit high quality (chlorine content 6 at.%, resistivity $200\ \mu\Omega\text{cm}$) TiN films at low deposition temperature (400°C) with good step coverage. In the ALD process, the precursors are introduced onto the substrates alternately. Between the reactant pulses the reactor is purged by an inert carrier gas. Due to these complicated gas switching sequences, the throughput rate of ALD is 1/30 of the normal CVD process.¹⁴⁾

In view of these issues, we propose a new CVD process, the flow modulation chemical vapor deposition (FMCVD),^{15,16)} to obtain high quality titanium nitride (TiN) films at low deposition temperature in a single CVD chamber. In the present work, we have investigated the performance of FMCVD process and found that FMCVD can provide superior film properties at low deposition temperature with sufficient throughput rate for mass production.

2. Concept of FMCVD

FMCVD is one of the advanced CVD processes for future ULSI devices, in which the flow rate of precursors are cyclically changed. This operating sequence may enhance surface adsorption/desorption of reacting species and control the nucleation on growing surfaces. These features contribute to uniform step coverage and fine grain size of deposited films. We can also combine systematic temperature control and total pressure control of FMCVD for further modification.

In the case of TiN-CVD from TiCl_4 and NH_3 , it is difficult to get both low residual chlorine concentration and good step coverage. The basic strategy to satisfy both demands is to deposit the TiN film at good step coverage condition and then carry out the chlorine reduction step. FMCVD is suitable for

this operation and it has superior characteristics to the post annealing process. The essential advantage of FMCVD over the post annealing process is the time constant required for reducing the chlorine in the film. As the chlorine reduction is controlled by diffusion of the reduction agent or chlorine containing species through the film, the reduction time, τ can be given as

$$\tau \propto \frac{L^2}{D}, \quad (1)$$

where L is the diffusion length, corresponding to the film thickness, and D is the diffusion coefficient of the reducing gas or chlorine containing species in the deposited film. When we deposit TiN films by FMCVD using N times cycle, the film thickness in one cycle is $1/N$ of normal CVD, which only requires $1/N^2$ reduction time. The total time constant required for reduction of the chlorine in the film can be given as

$$\tau' \propto \frac{\left(\frac{L}{N}\right)^2}{D} \times N. \quad (2)$$

The total time constant to reduce the chlorine in FMCVD can be obtained as

$$\tau' = \frac{\tau}{N}. \quad (3)$$

Equation (3) shows that the time constant for FMCVD is inversely proportional to N , and therefore increase of FM cycle number results in decrease of total process time, that is, the throughput rate is nearly the same as that of regular CVD processes with superior film properties.

In the present work, a detailed study on FMCVD TiN films from TiCl_4 and NH_3 has been carried out. We report FMCVD TiN films properties as a function of FM cycle number and deposition temperature.

3. Experimental

TiN was deposited in a cold-wall CVD reactor with a load-lock chamber. The wall temperature was kept at 180°C to prevent the adduct formation from TiCl_4 and NH_3 . The background pressure before deposition was about 10^{-7} Torr. TiCl_4 was supplied by the bubbling system using Ar as the carrier gas. The bubbler was in a thermobath at 60°C . The pressure in the bubbler was maintained at 760 Torr using the pressure transducer (MKS 624), the pressure regulation valve (MKS 148J) and the pressure controller (MKS 250). The tubes from the bubbler to the reactor were kept at 80°C to prevent the condensation of TiCl_4 . TiCl_4 and NH_3 were supplied into the reactor separately to prevent the adduct formation. The total pressure was 2 Torr and the initial concentrations of TiCl_4 and NH_3 were at 0.01 Torr and 0.5 Torr respectively, which led to good step coverage with high residual chlorine.¹⁰⁾ The sequence of gas flow was controlled by the computer, which was connected to the gas supply system (Fig. 1). A standard four-point probe technique was used to measure sheet resistances. The thickness of the films was analyzed by field emission-scanning electron microscopy (FE-SEM). The composition was investigated by X-ray photoelectron spectroscopy (XPS).

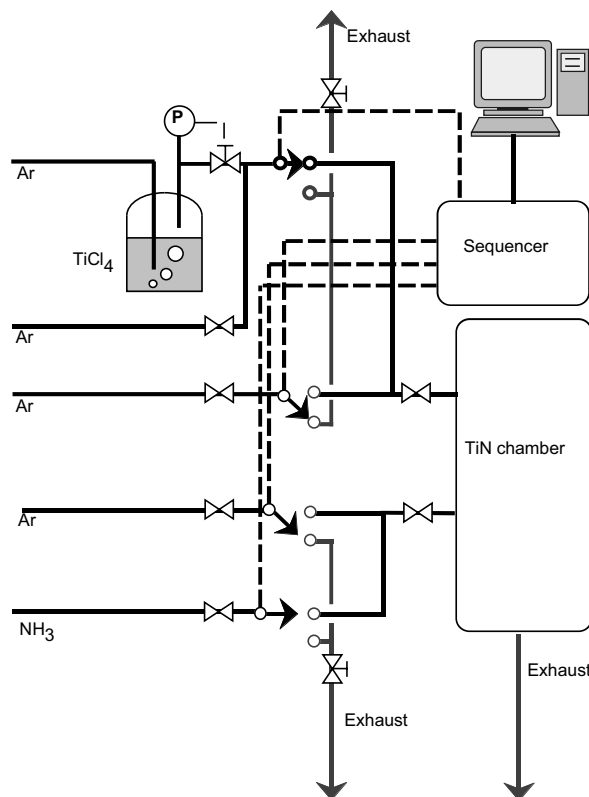


Fig. 1. Experimental system design.

Table I. Deposition sequences for the effect of FM cycle number.

Sample name	Deposition period (s) × cycle number	Reduction period (s) × cycle number
Normal	300×1	0
Post-annealing	300×1	200×1
FM2	150×2	100×2
FM5	60×5	40×5
FM10	30×10	20×10
FM20	15×20	10×20
FM100	3×100	2×100

4. Results and Discussion

4.1 The effect of FM cycle number

First, we investigated the effect of flow modulation (FM) cycle number at 380°C . Table I summarizes the deposition sequences. The normal CVD sample underwent no treatment after deposition, while the post-annealing sample was annealed in NH_3 atmosphere after deposition for 200 s. The FMCVD samples were prepared by applying the following procedure. First, TiN film was deposited from TiCl_4 and NH_3 for some period of time, and then TiCl_4 flow was switched to the exhaust system, while, the same amount of Ar gas flow was supplied into the chamber, so that the total pressure did not change during this sequence. The TiN film was thus annealed under NH_3 atmosphere during this period. This sequence was repeated for a certain number of times. The total deposition time and annealing time were fixed at 300 s and 200 s, respectively. Figure 2 shows the gas flow of the experimental procedure of FMCVD.

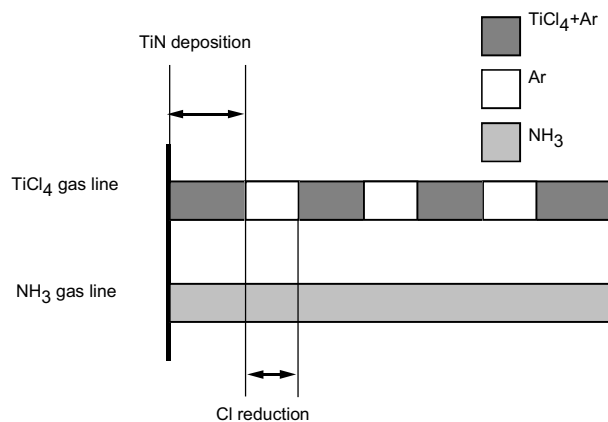


Fig. 2. Gas flow for the experimental procedure of FMCVD.

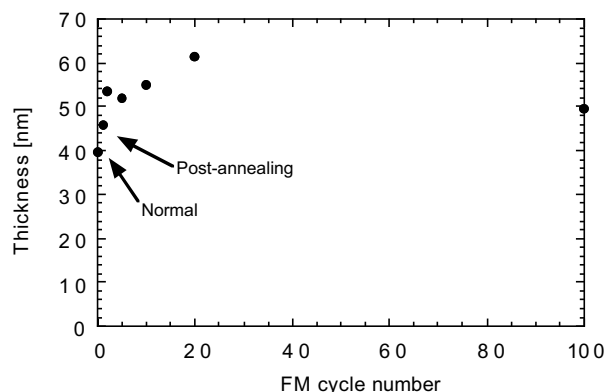


Fig. 3. The film thickness as a function of FM cycle number.

Figure 3 shows the film thickness of deposited films at 380°C as a function of FM cycle number. With increase of FM cycle number, the film thickness slightly increased. The same trend was observed at other deposition temperatures (410°C, 440°C). This result suggests that unreacted TiCl_4 still existed in the reactor, and subsequently TiN films grow during the chlorine reduction process. It is note worthy that the throughput of the FM100 process was the same as that of the post-annealing process.

Figure 4 shows the chlorine concentration in the films as a function of the FM cycle number. We can see a decrease of chlorine concentration in the films with an increase of FM cycle number, and the residual chlorine level of TiN films by FMCVD was much lower than that by normal CVD and post-annealing. This result suggests that the FM sequences with NH_3 easily reduced chlorine in the films, and thinner TiN films have advantage in decreasing chlorine.

Figure 5 shows the resistivity of the films as a function of FM cycle number. The resistivity decreased with FM cycle number and the lowest value was 250 $\mu\Omega\text{cm}$ for 100 FM cycles. This result is consistent with the chlorine concentration in the films as shown in Fig. 4.

These film properties show that FMCVD is superior to the post-annealing process, although the throughput rate is of the same level.

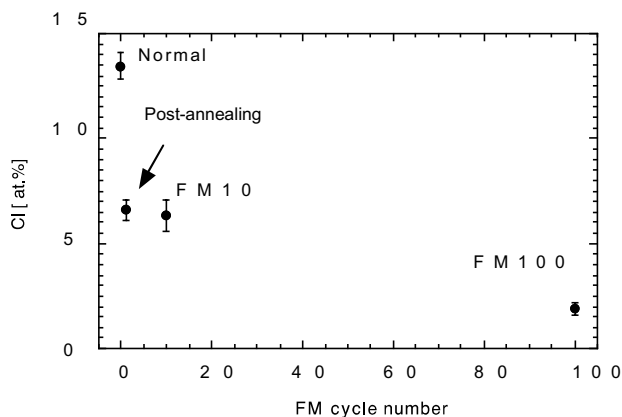


Fig. 4. Chlorine concentration in the films as a function of FM cycle number.

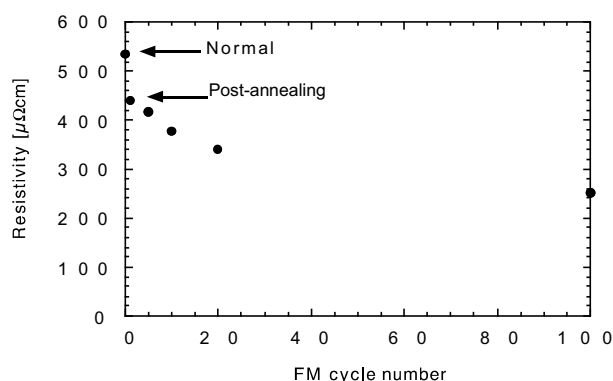


Fig. 5. Resistivity of the films as a function of FM cycle number.

4.2 The effect of reduction time in one cycle

From eq. (3), in the case of FM10, the total time required for chlorine reduction is 1/10 that of post-annealing, that is, 20 s. The reduction time of 2 s in each cycle should be equivalent to the 200 s post-annealing. The effect of reduction time in one cycle was investigated for the FM10 process. We changed the reduction period from 1 s to 20 s, while the deposition time in one cycle was maintained at 30 s.

The chlorine concentration and the resistivity of the films as functions of reduction time in one cycle are shown in Figs. 6 and 7, respectively. The residual chlorine concentration shown in Fig. 6 reaches almost the same level as that obtained by post-annealing with only 1 s of reduction time in one cycle. There is no apparent tendency in the decrease of residual chlorine concentration, while the resistivity is decreased, by increasing the reduction time in one cycle. These tendencies suggest that most of the chlorine exists at grain boundaries and is easily removed. The grains tend to coalesce during the reduction period and this coalescence may contribute to the reduction of resistivity by decreasing the voids between grains.

As predicted from eq. (3), the 2 s reduction time in one cycle of the FM10 process may be sufficient to obtain the same film properties obtained by 200 s post-annealing. That is, the total process time of the FM10 process becomes 320 s and if we use the FM100 process, 302 s may be sufficient. However, the shortest gas switching interval is 0.5 s in our system and

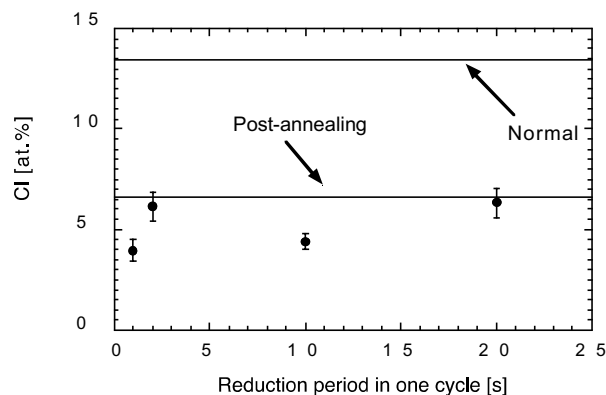


Fig. 6. Chlorine concentration in the films as a function of reduction time in one cycle.

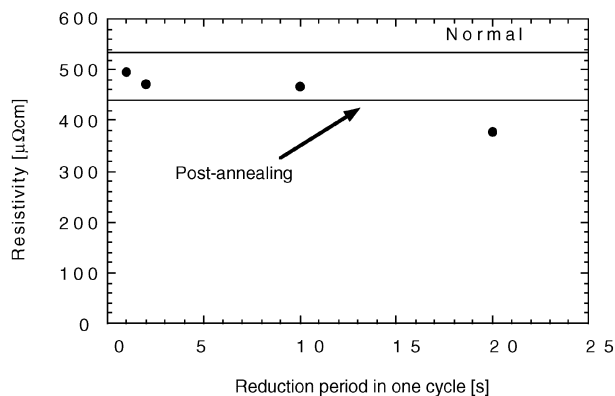


Fig. 7. Resistivity of the films as a function of reduction time in one cycle.

the shortest FM100 process requires a total of 350 s.

These results demonstrate that the throughput rate of FM-CVD is nearly of the same level as that of the regular CVD processes resulting in superior film properties.

4.3 The effect of deposition temperature

To investigate the effect of deposition temperature, three types of samples were prepared at different deposition temperatures (330–440°C). The chlorine concentration and the resistivity of the three types of films as functions of the deposition temperature were investigated as shown in Figs. 8 and 9, respectively. The resistivity of the films decreased with increase of deposition temperature and the value for the FM100 sample was the lowest for each deposition temperature. Chlorine concentration also decreased with deposition temperature, but it did not decrease above 380°C in the case of FMCVD samples. A lower chlorine concentration causes the decrease of resistivity in each type of sample with increase of deposition temperature. From the result of chlorine concentration, it is noted that chlorine is easily reduced using FM-CVD, but it still exists at 2 at.% level. It is considered that the major residual chlorine exists at the grain boundaries and can be easily reduced by NH_3 , but minor chlorine is strongly bonded to titanium, and hence is difficult to remove.^{12,17–19)}

It is note worthy that the value for the FM100 sample grown at 380°C is lower than that for the normal and post-annealed samples deposited at higher temperatures (410°C, 440°C).

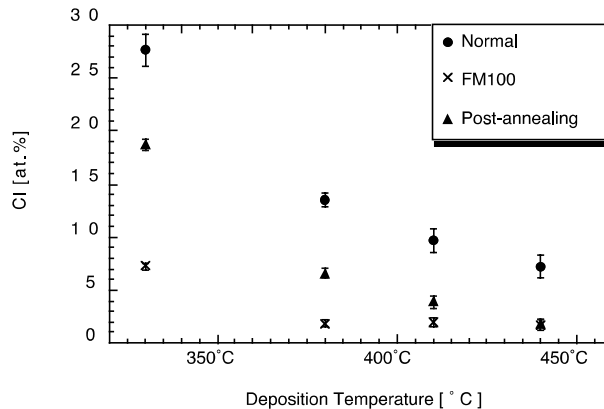


Fig. 8. Chlorine concentration of the three types of films as a function of deposition temperature.

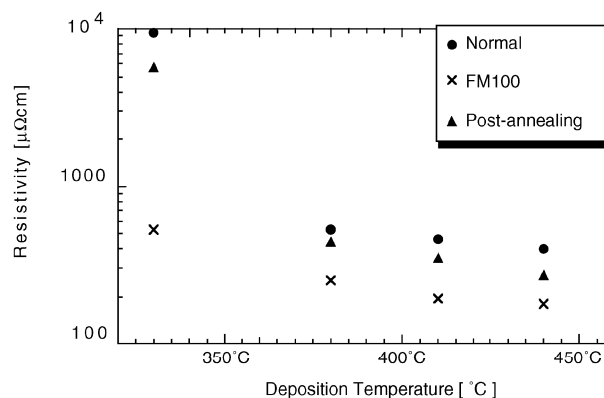


Fig. 9. Resistivity of the three types of films as a function of deposition temperature.

This deposition temperature dependence suggests that FM-CVD appears to be an effective method to obtain TiN films of low resistivity and low chlorine concentration at low deposition temperature.

4.4 Step coverage

The step coverage of films prepared by FMCVD and normal CVD at 380°C was investigated. In this experiment, we performed the FM sequences 500 times to obtain thick TiN films for step coverage observation. The deposition and reduction times in one cycle were 3 s and 2 s, respectively. The deposition time of the normal CVD process was 1500 s. Figure 10 shows the cross-sectional SEM image of TiN films in high-aspect ratio trench. (top width: 1.6 μm, bottom width: 0.9 μm, depth: 6.4 μm) As shown here, we could achieve excellent step coverage using both methods. The values of resistivities were 250 μΩcm (FMCVD) and 550 μΩcm (normal CVD). This is a demonstration of the FMCVD process which provides excellent step coverage with better film properties.

5. Conclusions

We propose a new CVD process, the flow modulation chemical vapor deposition (FMCVD) process, to obtain high quality (good step coverage, low resistivity and low residual chlorine concentration) TiN films at low deposition tempera-

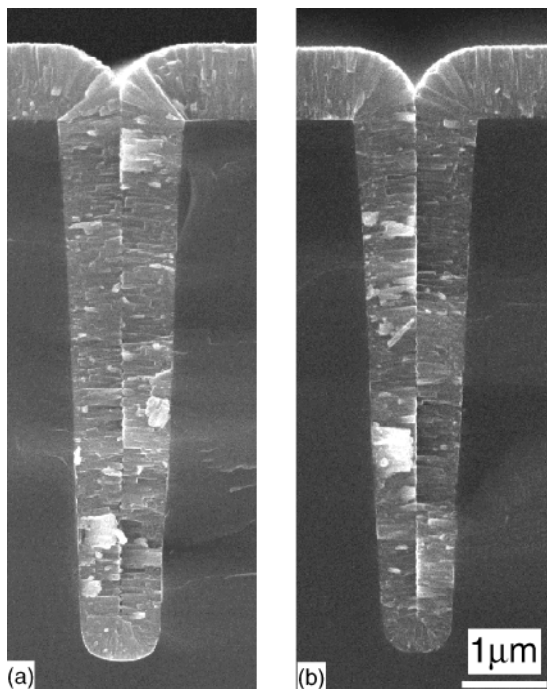


Fig. 10. Cross-sectional SEM image of TiN films prepared by (a) FMCVD and (b) Normal CVD in high-aspect ratio trench. (top width: $1.6\text{ }\mu\text{m}$, bottom width: $0.9\text{ }\mu\text{m}$, depth: $6.4\text{ }\mu\text{m}$)

ture in a single CVD chamber. In FMCVD, we just switch the TiCl_4 flow to the Ar flow cyclically and this sequence creates sequential deposition and reduction processes, such as the deposition of TiN films followed by chlorine reduction.

The chlorine concentration and resistivity of the films decreased with an increase of FM cycle number, and the values for TiN films by FMCVD were much lower than those by normal CVD and post-annealing. This result suggests that FM sequences with NH_3 easily reduced chlorine in the films, and thinner TiN films have the advantage of decreased chlorine. From the effect of chlorine reduction time in one cycle, it appears that diffusion phenomena control the chlorine reduction in the TiN films, which explains the superiority of the FMCVD process to the post-annealing process. The deposition temperature dependence suggests that the FMCVD process appears to be an effective method to obtain low resistivity and chlorine concentration TiN films at lower deposition temperature.

We determined that the film properties and the throughput of the FMCVD process were better than those of the post-annealing process. Using this FMCVD process, we could achieve low resistivity ($250\text{ }\mu\Omega\text{cm}$) and low residual chlorine concentration (2 at.%) films with uniform step coverage at low deposition temperature (380°C).

A cyclic operation or a multi step operation as in FMCVD may be the key to achieve fine structure control for future ULSI fabrication.

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