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Effect of Partial Pressure of $TiCl_4$ and NH_3 on Chemical Vapor Deposition Titanium Nitride (CVD-TiN) Film Cl Content and Electrical Resistivity

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Chemical vapor deposition titanium nitride (CVD-TiN) films were deposited from $TiCl_4$ and NH_3 at 410°C, that was sufficiently low for making ULSI multi-level interconnections. We investigated the Cl content and resistivity of CVD-TiN films as a function of $TiCl_4$ and NH_3 partial pressure (P_{TiCl_4}, P_{NH_3}). We found that Ti/(Ti + N) ratio was almost constant against different P_{TiCl_4} and P_{NH_3} conditions, while the resistivity and residual chlorine concentration were sensitive to these conditions. The lowest resistivity of 480 μΩ·cm and the lowest Cl concentration of 2% were achieved in the condition of the step coverage of 96% and the throughput of 16 nm/min when $P_{TiCl_4} = 0.01$ Torr, and $P_{NH_3} = 0.25$ Torr, respectively. These values may be further improved by using flow modulation method. [DOI: 10.1143/JJAP.43.L519]

KEYWORDS: titanium tetrachloride ($TiCl_4$), ammonia (NH_3), titanium nitride (TiN), CVD, Cl content, film resistivity, partial pressure

Titanium nitride (TiN) is widely used for wear-resistant coatings,[1] contact and barrier layers in metal-oxide semiconductor (MOS) circuits,[2–5] for diffusion-barrier layers in either Al/W[6,7] or Cu[8] interconnects, and for oxygen diffusion-barrier layers[9] in ULSI components. Uniform deposition onto high aspect-ratio via holes is required in ULSI components, which can be achieved with titanium nitride chemical vapor deposition (TiN-CVD) using $TiCl_4$ and NH_3. Deposition at a high temperature (600–850°C) forms films with low residual Cl (0.1–2.7%) and low electrical resistivy (80–133 μΩ·cm),[10–13] however, deposition temperatures below 450°C are required for TiN-CVD, because of the poor thermal stability of low-k intermetal dielectrics. TiN films deposited from $TiCl_4$ and NH_3 below 450°C are unsuitable because they typically have high electrical resistivity over 500 μΩ·cm and high Cl content of 7–8%.[12–14] Hamamura *et al.*[14] developed flow modulation CVD (FMCVD) to deposit TiN films from $TiCl_4$ and NH_3 at temperatures below 450°C and with acceptable film properties. FMCVD uses multiple, alternating steps of TiN-CVD followed by several seconds of NH_3 annealing ($P_{NH_3} =$ 0.25 Torr). The annealing reduces both the Cl content and the film resistivity. This permits deposition of TiN films with low electrical resistivity and low residual Cl content at temperatures below 450°C. FMCVD can also be used for deposition of ternary systems[15–17] that is required for Cu interconnect lines.

As the first work on TiN-FMCVD by Hamamura *et al.* was carried out by using the fixed deposition conditions, such as partial pressure of $TiCl_4$ (P_{TiCl_4}), NH_3 (P_{NH_3}) and substrate temperature (T_{sub}), we investigated the growth rate kinetics of TiN-CVD by changing P_{TiCl_4} and P_{NH_3} in our previous work.[18] We found that the growth rate followed the rate equation known as the Eley-Rideal type reaction mechanism, in which only $TiCl_4$ adsorbed on the surface and NH_3 reacted from the gas phase. When P_{TiCl_4} was higher than 0.02 Torr, the surface coverage of $TiCl_4$ was saturated and did not show P_{TiCl_4} dependency on the film growth rate, but the increase of P_{NH_3} resulted in higher growth rate with the power of 2. The step coverage analysis showed that the sticking probability of $TiCl_4$ at 1st-order reaction regime had 2nd-order dependency as a function of P_{NH_3}.

In this study, we investigated the effect of P_{TiCl_4} and P_{NH_3} on the Cl content and electrical resistivity of TiN films deposited at temperatures below 450°C to establish best deposition condition of TiN-CVD for ULSI barrier application. The film properties obtained under the best condition may be used for FMCVD to make further improvement of film properties. We used a showerhead type CVD reactor with warm-wall. Details of the reactor system are given elsewhere.[18] To prevent adduct formation, $TiCl_4$ and NH_3 were introduced into the reactor as separate streams. The heater temperature was set to 650°C, resulting in a temperature of about 410°C at the surface of the substrate. TiN films whose thicknesses were 50–100 nm were deposited onto Si wafers coated with 100 nm thermal oxide films. Field emission scanning electron microscopy (FE-SEM, JEOL 6340F) was used to measure the film thickness. The film composition such as Cl content was measured by using X-ray photoelectron spectroscopy (XPS, ULVAC-ϕ1600C). XPS measurements were also used to determine the Ti/(Ti + N) ratio.

CVD-TiN films were deposited at $P_{NH_3} = 0.25$, 0.5, and 1.0 Torr, and P_{TiCl_4} was varied from 0.005 to 0.07 Torr. The total pressure was kept at 2 Torr by using Ar as the balance gas. Figure 1 shows the film Ti/(Ti + N) ratio vs P_{TiCl_4} and P_{NH_3}, and indicates that the Ti/(Ti + N) ratio had a constant value of about 0.5 (i.e., Ti:N = 1:1), independent of both P_{TiCl_4} and P_{NH_3}.

Figure 2 shows the electrical resistivity of TiN films vs P_{TiCl_4} and P_{NH_3} at $T_{sub} = 410$°C, and indicates that the resistivity increased with increasing P_{TiCl_4}. Figure 3 shows the electrical resistivity vs film Cl content. Figure 3 indicates that the electrical resistivity was nearly proportional to film Cl content, which is consistent with the results of Leutenecker *et al.*[19] Our previous work showed that for $P_{TiCl_4} <$ 0.01 Torr, the film growth rate was proportional to P_{TiCl_4}, and for $P_{TiCl_4} \geq 0.02$ Torr the film growth rate became saturated. This indicates that the film Cl content may be independent of P_{TiCl_4} when it exceeds 0.02 Torr, because the growing surface becomes saturated with adsorbed $TiCl_4$. The reason the film Cl content and electrical resistivity increase with increasing P_{TiCl_4} may be adduct (NH_4Cl) formation in the gas phase and its subsequent adsorption, the

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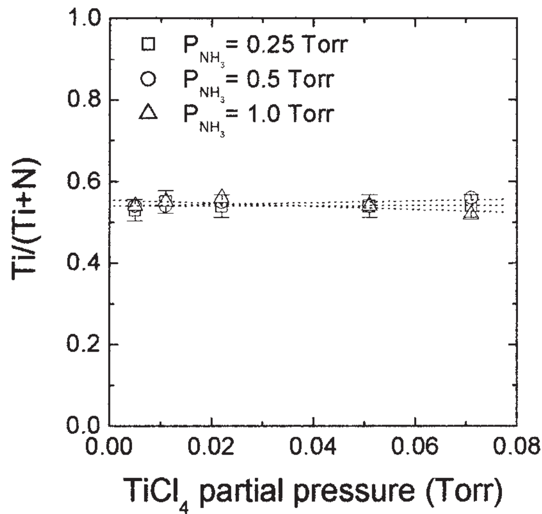

Fig. 1. Ti/(Ti + N) ratio vs $TiCl_4$ and NH_3 partial pressures.

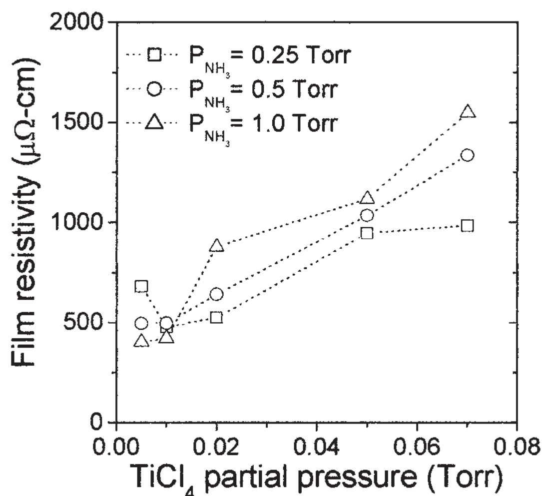

Fig. 2. Film resistivity vs $TiCl_4$ and NH_3 partial pressures.

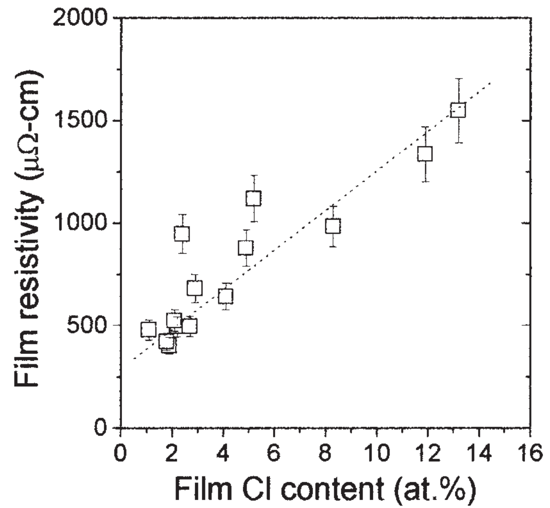

Fig. 3. Film resistivity vs Cl content.

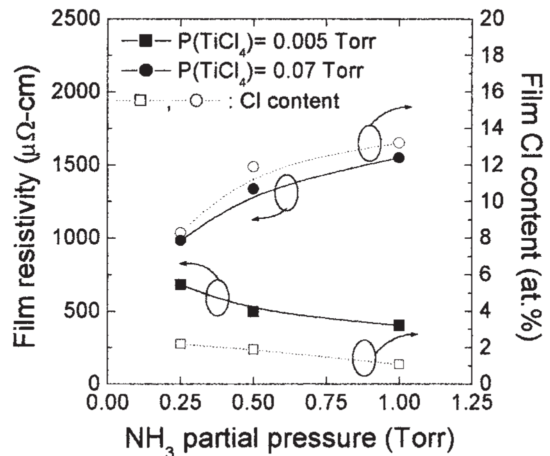

Fig. 4. Film resistivity and Cl content vs $TiCl_4$ and NH_3 partial pressures.

rate of which increases with increasing P_{TiCl_4}.

Figure 4 shows the film Cl content and resistivity vs P_{TiCl_4} and P_{NH_3}. Figure 4 indicates that for $P_{TiCl_4} = 0.005$ Torr the film Cl content and resistivity decreased with increasing P_{NH_3}, but that for $P_{TiCl_4} = 0.07$ Torr the film Cl content and resistivity increased with increasing P_{NH_3}. The reason for this different behavior is as follows.

For $P_{TiCl_4} < 0.01$ Torr, the film growth rate is proportional to P_{TiCl_4}.[18] In this regime the surface sticking coefficient is proportional to ${P_{NH_3}}^2$.[18] Increasing P_{NH_3} therefore increases the sticking coefficient, which increases the film formation rate, and causes mass transport from the gas to the surface to become the rate-limiting step. Therefore, Cl reduction was enhanced at $P_{TiCl_4} = 0.005$ Torr by increasing P_{NH_3}, because the TiN film growth rate was limited by mass transport rate. For $P_{TiCl_4} \geq 0.02$ Torr, the film growth rate was independent of P_{TiCl_4} and was proportional to ${P_{NH_3}}^2$.[18] Cl reduction by NH_3 may be a 1st-order reaction and Cl incorporation rate may be proportional to the growth rate, which is proportional to ${P_{NH_3}}^2$. Therefore, for $P_{TiCl_4} \geq 0.02$ Torr the residual Cl concentration and resistivity increases with increasing P_{NH_3}.

In summary, TiN films formed at 410°C had a Ti:N ratio of about 1:1. Increasing P_{TiCl_4} increased the film Cl content and electrical resistivity, independent of P_{NH_3}. For $P_{TiCl_4} < 0.01$ Torr, the Cl content and electrical resistivity decreased with increasing P_{NH_3}. For $P_{TiCl_4} \geq 0.02$ Torr, the resistivity increased with increasing P_{NH_3}, because although the Cl reduction by NH_3 may be proportional to P_{NH_3}, the film growth rate was proportional to ${P_{NH_3}}^2$.

The values of P_{TiCl_4} and P_{NH_3} should be optimized for uniform step coverage, low electrical resistivity, low Cl content, and high throughput. The lower P_{TiCl_4} resulted in lower Cl content and lower film resistivity. However, for $P_{TiCl_4} < 0.01$ Torr resulted in poor step coverage and lower deposition rate. For $P_{TiCl_4} \geq 0.02$ Torr, the growth rate is saturated, while the resistivity and film Cl content increases by increasing $P_{TiCl_4} \geq 0.02$. Thus, P_{TiCl_4} should be in the range of 0.01–0.02 Torr. Increasing P_{NH_3} increased the throughput, but also increased the resistivity of the film. When P_{NH_3} is less than 0.25 Torr, the film resistivity and Cl content increases due to poor reduction effect. P_{NH_3} should be 0.25 Torr to realize lower resistivity. The best condition may be $P_{TiCl_4} = 0.01$ Torr and $P_{NH_3} = 0.25$ Torr with the step coverage of 96%, and the throughput of 16 nm/min, which may be high enough for barrier layer deposition. The film resistivity and film Cl content under this condition are

480 μΩ·cm (film thickness is 80 nm) and 2%, respectively. These values can be further reduced by employing FMCVD method.

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