

Invited**Growth and Properties of LPCVD TiN for ULSI**

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This paper reviews recent studies of the low-temperature, low-pressure, chemical vapor deposition of titanium nitride thin films for ULSI applications. In addition to the comprehensive studies available for films deposited from TiCl_4 , films derived from organometallic precursors are discussed, and plasma-enhanced techniques are also mentioned briefly. The effectiveness of the resulting conformal films as diffusion barriers is described, along with the influence of the residual chlorine (for films from TiCl_4).

1. INTRODUCTION

Recent advances in very high density integrated circuits (ULSI) have required multilevel metallization schemes. Since this, in general, means many contacts between dissimilar conductors and semiconductors (i.e., silicon, aluminum, titanium silicide, platinum silicide) and subsequent high temperature annealing, barrier films have become an integral part of such circuits. For some time now, sputtered TiW has been used, where tungsten provides the barrier and a small quantity of titanium is added to improve adhesion. A better barrier film, with good adhesion, has been found to be reactively-sputtered TiN.

In both cases, the step coverage of either film is very poor, especially for high aspect ratio contact or via holes (>2:1). When film conformality is a critical issue, CVD TiN becomes a viable alternative, since as will be shown, these films can be almost 100% conformal. Unfortunately, the traditional CVD TiN process involves the reaction between $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$ at $\sim 1000^\circ\text{C}$, and this is much too high a temperature to be practical in ULSI where thermal budgets must be kept to a minimum.

In this paper, therefore, we will review lower temperature CVD TiN processes ($200\text{--}700^\circ\text{C}$) that will hopefully prove to give effective conformal barrier films.

2. CVD TiN FILMS FROM TiCl_4 and NH_3

Most investigators studying CVD TiN recognized early on that reacting TiCl_4 with NH_3 rather than N_2 and H_2 should lead to a lower temperature process. Unfortunately, efforts along these lines were not particularly fruitful because TiCl_4 and NH_3 react at room temperature to form a solid adduct. This made it difficult to mix the gases and introduce them to the

reactor without gas phase nucleation. Researchers at Motorola¹⁾ and Harvard²⁾ were the first to observe that these two gases neither react in the gas phase or deposit any TiN film on surfaces in the temperature range of $\sim 250\text{--}350^\circ\text{C}$. Based on this fact, the Motorola group developed a low-pressure, hot-tube system at 700°C , and the Harvard researchers developed an atmospheric pressure, cold-wall tube reactor and deposited films at $500\text{--}650^\circ\text{C}$. The reaction scheme (highly simplified) was:



More recently, a number of studies have demonstrated that this reaction could be carried out in a low-pressure, cold-wall, single-wafer reactor³⁻⁶⁾ at similar temperatures and high deposition rates ($500\text{--}1000 \text{ \AA}/\text{min}$). One group⁵⁾ used a reactor with warm (rather than cold) walls ($\sim 250\text{--}350^\circ\text{C}$) to prevent deposition on the walls.

Film Chemistry:

In general, investigators have found that stoichiometric (1:1) films are formed by this process with small quantities of impurities. The most important of these impurities is chlorine, which can be over 5 atomic percent. As shown in Fig. 1, its concentration is minimized by deposition at higher temperatures. A few atomic percent oxygen is also typically seen, depending on how well the system has been purged of water vapor or residual air. As one would expect, the higher the oxygen content, the higher the deposition temperature. Finally, there can be as much as 5% hydrogen incorporated in the film⁴⁾.

Some attempts have been made to anneal these films at high temperature (700°C) to lower the chlorine content. Apparently, because the chlorine is tightly bound into the film, one ends up with less chlorine by

depositing at the higher temperature (700°C) than by depositing at lower temperature (500°C) and annealing³).

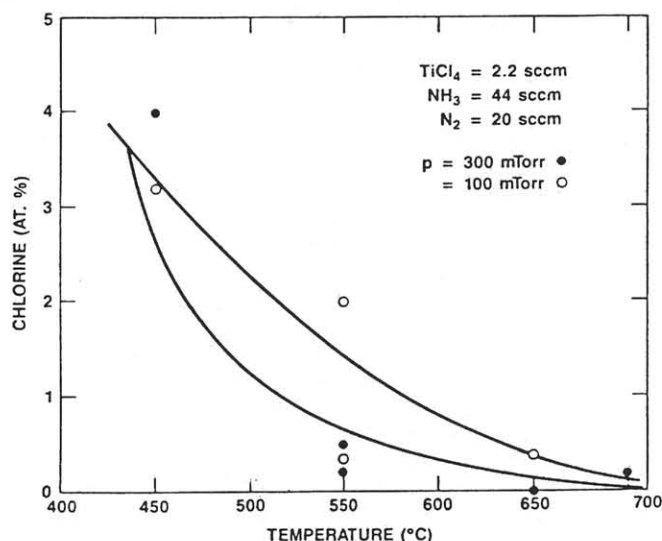


Fig. 1 Chlorine content as a function of temperature⁴).

Film Resistivity:

Although resistivity of these films is considerably higher than bulk TiN ($18 \mu\Omega\text{-cm}$), it can be kept quite low when depositions are done at higher temperatures. Values from 100 to 300 $\mu\Omega\text{-cm}$ are typical, with the lowest values observed at the highest temperatures.

Behavior as Diffusion Barrier:

When considering these films as diffusion barriers between silicon and aluminum, it is important to know if the chlorine impurity will cause corrosion problems. Two studies have shown^{4,7}) that a Si/TiN/Al structure heated to 500°C for 30 minutes shows no evidence of breakdown. Another investigation⁸) looked at metal (TiN/Al) serpentine continuity structures that were subjected to autoclave stress for 72 hours. No differences in resistance were found.

The next concern relates to contact resistance. Placing a barrier film between two conductors must first keep them from diffusing into each other when subjected to thermal stress, but it must also allow low contact resistance between them. This is especially important for ULSI with very small contacts. In one experiment, TiN was deposited directly onto silicon (p^+ - boron doped to $5 \times 10^{19}/\text{cm}^2$), and the contact resistance was measured to be $\sim 2.2 \times 10^{-6} \Omega\text{-cm}$ after a 500°C bake⁴). In another study⁹), the TiN was deposited onto titanium silicide (salicide) contacts, and the results are shown in Fig. 2. Even lower values were found in the Motorola study⁸).

Finally, many contact diodes were examined to see if a reverse bias voltage showed any excess leakage. Results found were that annealing to 525°C did not produce any significant leakage⁸).

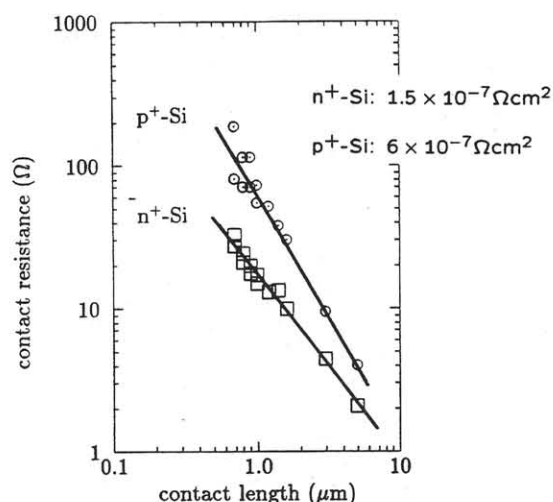


Fig. 2 Contact resistance of 0.7- μm contacts. TiN on TiSi⁹).

Conformal Film Coverage:

The possibility of depositing very conformal TiN film into high aspect ratio holes is the prime reason for current interest in this technology. A number of studies^{3,4,6}) have shown that under the correct flow conditions conformality can be outstanding, even for sub-micron trenches of aspect ratio $\sim 7:1$ ⁸). It is also possible to completely fill sub-micron contact holes.

3. MOCVD PROCESSES

Rather than use TiCl_4 as the Ti precursor in CVD TiN, one could use a metal-organic molecule, thereby avoiding chlorine contamination. Two choices are available. One possibility would be to use tetrakis (dimethylamido) titanium, $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ and pyrolyze it to yield TiN, since the molecule already contains nitrogen. It has been shown that a more successful approach is to reduce it with NH_3 ¹¹). In this case, deposition in an atmospheric-pressure, cold-wall tube reactor at 200-400°C yielded reasonably pure stoichiometric films. A second approach would be to use bis-cyclopentadienyltitanium, $(\text{C}_5\text{H}_5)_2\text{Ti}$, again with NH_3 ¹²). Here, reasonably pure films are reported at deposition temperatures of 450°C in a low-pressure, cold-wall reactor. If either film, when deposited at temperatures $\leq 400^\circ\text{C}$, can be shown to have attributes similar to the higher temperature films deposited from TiCl_4 , then they are candidates to be used over aluminum as well as silicon.

4. PECVD PROCESSES

Finally, deposition temperatures can be lowered using a glow discharge. Although a number of studies have shown this possible with $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$ or $\text{TiCl}_4 + \text{NH}_3$, they all result in a great deal of chlorine incorporation. One exception has been reported where a $\text{TiCl}_4 + \text{NH}_3$ mixture is excited at 13.56 MHz, and

the chlorine content of the film is reported to be quite low at 400°C¹³). The behavior of the chlorine concentration with substrate temperature is shown in Fig. 3.

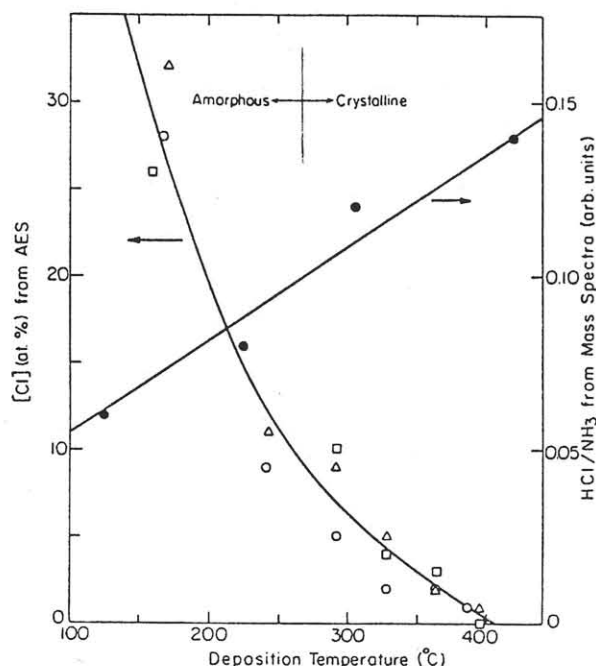


Fig. 3 Chlorine content of TiN films formed by PECVD¹³).

5. CONCLUSIONS

Comprehensive studies have indicated that TiN films formed at moderate temperatures from $\text{TiCl}_4 + \text{NH}_3$ are good quality diffusion barriers for ULSI circuits. Lower temperature depositions are possible by PECVD, and lower temperature as well as zero chlorine films can be made from organometallic precursors. Whether these lower temperature films are suitable as diffusion barriers and can be conformally deposited over high aspect ratio contact and via holes, remains to be demonstrated.

6. REFERENCES

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