

Fig. 16. Contact resistance measurements (a), (c) with and (b), (d) without integrated plasma cleaning: (a), (b) MOCVD TiN; (c), (d) TiCl<sub>4</sub> TiN.

(5) Considerable promise lies in other MOCVD processes, and in chemistries using TBA, MH and other similar sources for nitrogen.

(6) Integrated precleaning is important for achieving acceptable contact resistance.

(7) A future challenge will be to develop a CVD Ti or similar contact resistance adjustment film, or to integrate sputtered Ti in a vacuum cluster tool.

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# Properties of chemical-vapor-deposited titanium nitride

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## Abstract

The attributes and limitations of several chemical-vapor-deposited TiN chemistries are discussed:  $\text{TiCl}_4 + \text{NH}_3$  (ammonia) +  $(\text{CH}_3)\text{HNNH}_2$  (methylhydrazine, MH), or  $(\text{CH}_3)_3\text{CH}_2\text{N}$  (tert-butylamine, TBA) and  $\text{NH}_3 + \text{Ti}(\text{N}(\text{CH}_3)_2)_4$  (tetrakis dimethylamido-titanium, DIMAT). Problems associated with native oxide removal and surface cleaning are also discussed, along with results from integrating preclean and chemical vapor deposition in a clustered single-wafer platform.

## 1. Introduction

TiN was originally used for tool coatings in which wear resistance was important [1, 2]. Gold in color, TiN films are extremely hard, have a high melting point of nearly 3300 °C and excellent thermal stability. In most of these early applications, TiN films were deposited by chemical vapor deposition (CVD) from  $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$  gas mixtures at temperatures above 1000 °C.

The emergence of reactive physical vapor deposition (PVD) has led to TiN films being deposited at temperatures below 500 °C. At these lower deposition temperatures, the use of TiN for silicon microelectronic technology has become attractive, because of the material's excellent diffusion barrier characteristics, very good electrical conductivity and excellent adhesion/glue layer performance. However, one key limiting issue with PVD TiN is poor step coverage, especially for submicrometer-sized geometries. This has led to the recent development of collimated sputtering, extending the applicability of PVD TiN down to 0.35  $\mu\text{m}$  technologies. Nevertheless, CVD TiN must be used if better step coverage is needed or to extend the use of TiN below 0.35  $\mu\text{m}$  in size.

Two basic approaches for TiN CVD are plasma-enhanced CVD (PECVD) and thermal CVD. A variety of gas chemistries can be used in thermal CVD to deposit at desired low temperatures, and this is the focus of this paper.

## 2. Film properties and process chemistries

TiN films are very stable over a broad compositional range, yet the film performance and properties depend

critically upon the film composition (N/Ti ratio) and impurities. The structural consequence of compositional variation is an excess of either sublattice Ti or N. Examples illustrating how PVD TiN film properties vary with the N/Ti ratio are shown in Fig. 1 for the parameters of resistivity, stress, lattice parameter, hardness and density. Reactively sputtered films are often Ti-rich in composition and the excess Ti can diffuse into Al alloys. Precise control of the PVD parameters is required to maintain an N/Ti ratio of nearly unity. It should be noted from the curves that, when the N/Ti ratio of 1.0 is achieved, there are minimum values of the film resistivity and stress, and maximum values of the lattice parameter, hardness and density. This film stoichiometry is ideal for use as a diffusion barrier. In a thermal CVD TiN film, the N/Ti ratios usually are between 0.95 and 1.05, irrespective of the process chemistry used, making this technique very attractive for producing high quality stoichiometric compositions.

For state-of-the-art device applications of TiN films, TiN step coverage of nearly 100% is needed for deep, narrow submicrometer contacts. To achieve optimum film performance, the following properties are required: a stoichiometric N/Ti ratio of nearly unity; resistivity < 100  $\mu\Omega\text{ cm}$ ; low chlorine and oxygen concentrations; a mass density > 5  $\text{g cm}^{-3}$ ; good film uniformity of less than 5%; low particle counts. Coupled with the film deposition process is the need to ensure a low contact resistance to  $p^+$  or  $n^+$  contacts, through a proper precleaning technique.

For CVD TiN to be successful in manufacturing, the process must be very reproducible and the key parameters affecting the film properties characterized. To date, the best understood CVD TiN process uses the  $\text{TiCl}_4 + \text{NH}_3$  chemistry.

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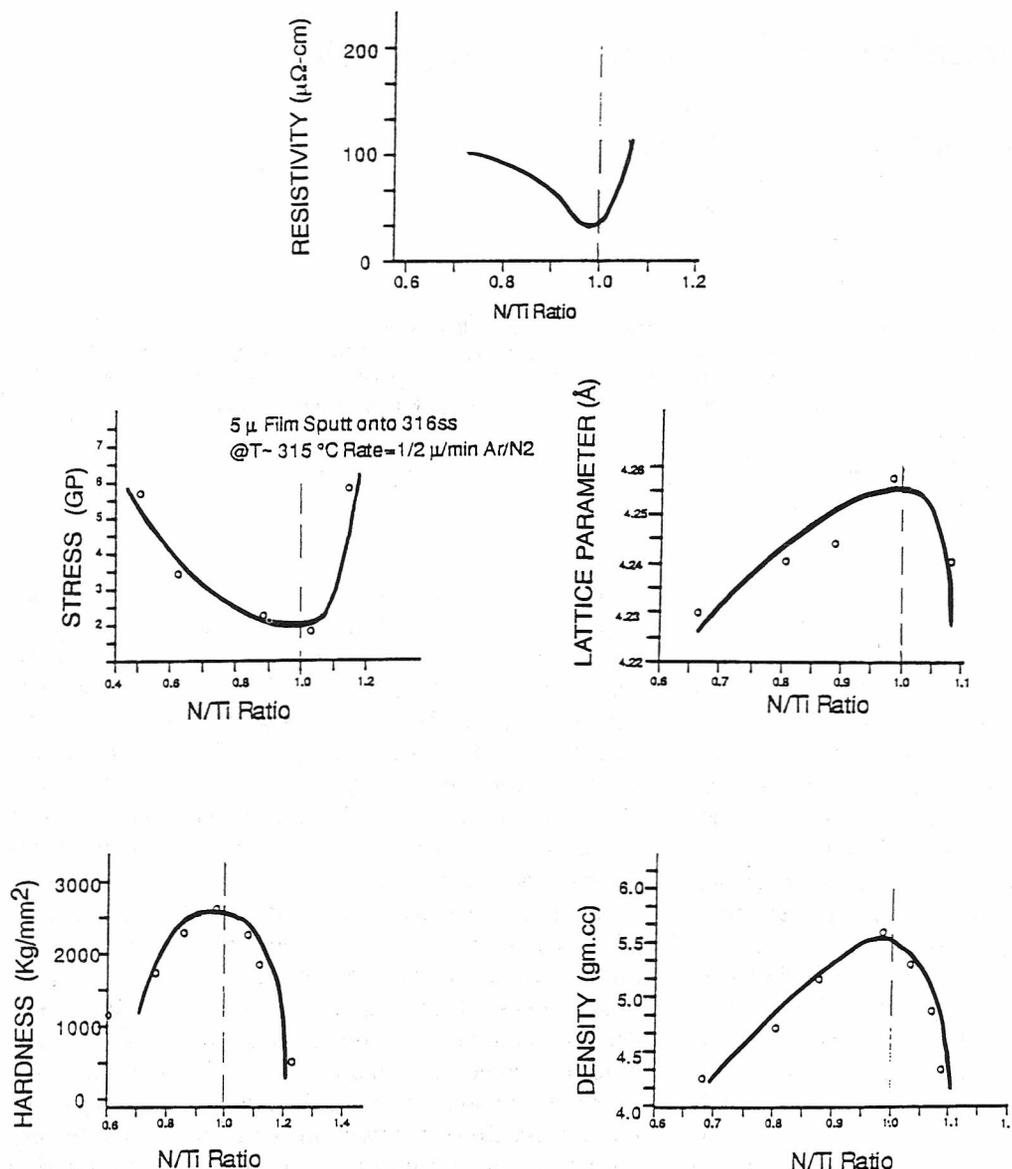


Fig. 1. Film resistivity, stress, lattice parameter, hardness and mass density *vs.* stoichiometry [3].

### 2.1. $\text{TiCl}_4 + \text{NH}_3$

The  $\text{TiCl}_4 + \text{NH}_3$  reaction is typically represented by

$$6\text{TiCl}_4 + 8\text{NH}_3 \longrightarrow 6\text{TiN} + 24\text{HCl} + \text{N}_2$$

This reaction is thermodynamically favorable above  $320^\circ\text{C}$ . However, processing is typically above  $600^\circ\text{C}$ , in order to achieve acceptable film properties. There are numerous publications on this chemistry and the reported film characteristics are similar [3–6].

The motivating factor in using CVD TiN over PVD TiN films is the improved step coverage of high-aspect-ratio contact structures. When deposition occurs in the surface reaction-rate-limited regime, high step coverage is achieved. However, if deposition occurs in

the gas phase diffusion-limited regime, poorer step coverage results. Data published for  $\text{TiCl}_4 + \text{NH}_3$  in the range  $450\text{--}750^\circ\text{C}$  show deposition to be in the surface reaction-rate-limited regime, with activation energies between 0.44 and 0.53 eV, as reported by Buiting *et al.* [4] and Price *et al.* [5], and shown in Fig. 2.

The effect of the  $\text{NH}_3$  and  $\text{TiCl}_4$  partial pressures on the deposition rate is shown in Fig. 3, as taken from publications by Srinivas *et al.* [8] and Selbrede [9].

It has been shown that, when the density of TiN is kept above  $5\text{ gm cm}^{-3}$ , the N/Ti ratio is usually between 0.9 and 1.05. Yokoyama *et al.* [10] reported on depositions in the range  $500\text{--}700^\circ\text{C}$  using a single-wafer low pressure CVD system. All the films had an N/Ti ratio

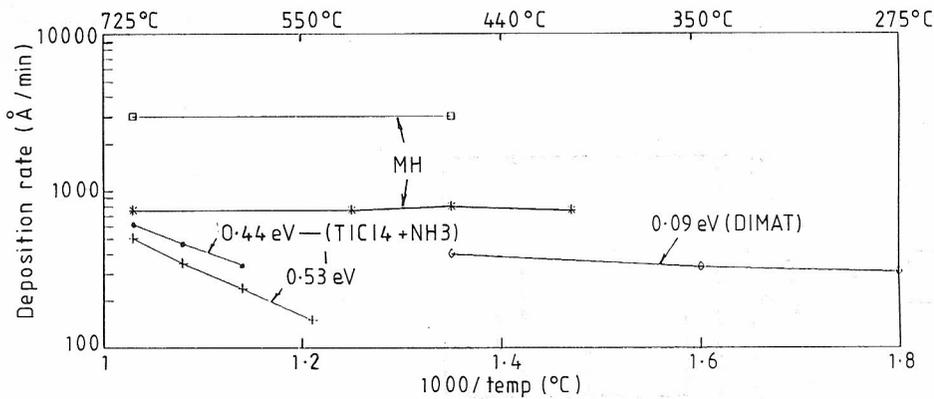


Fig. 2. CVD TiN deposition rate *vs.* reciprocal temperature from various chemistries: ●, Srinivas; +, Genus; \*, Suzuki (+MH 10); □, Suzuki (+MH 60); ◇, Raaijmakers (DIMAT+). TiCl<sub>4</sub> + NH<sub>3</sub> unless noted [5-7].

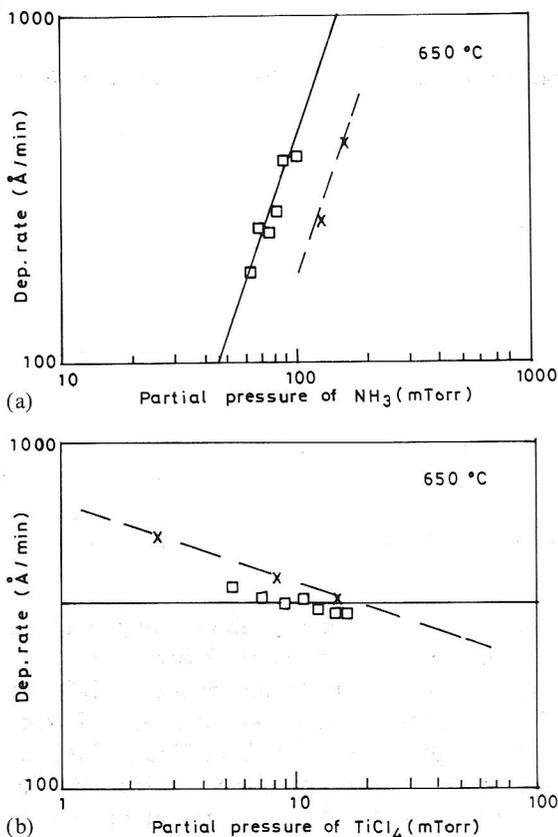


Fig. 3. Log CVD TiN deposition rate *vs.* partial pressures of (a) NH<sub>3</sub> and (b) TiCl<sub>4</sub>; □, ref. 8; ×, ref. 9.

of nearly 1.0 over this broad temperature range (Fig. 4). They also reported the dependence of the preferred TiN crystallographic orientation on the deposition temperature. At 500 °C, the dominant grain orientation was <200>, while it was <111> at 700 °C, as shown in Fig. 5. A similar observation was made Buiting and Otterloo who observed <200> grains at high partial pressures, of TiCl<sub>4</sub> and <111> grains at lower partial

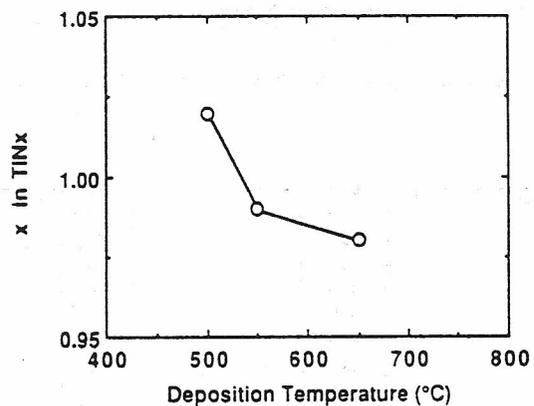


Fig. 4. As-deposited CVD TiN N/Ti ratio, using TiCl<sub>4</sub> + NH<sub>3</sub> chemistry [10].

pressures, as shown in Fig. 6 [11]. TiN has the NaCl crystal structure, with the phase diagram shown in Fig. 7 [12].

A low TiN film resistivity is desirable, because it improves the conductance of an interconnect. Comparative results of the TiN film resistivity *vs.* the deposition temperature are shown in Fig. 8. For all cases, deposition at temperatures above 675 °C was required to achieve an as-deposited film resistivity below 200 μΩ cm. To achieve less than 100 μΩ cm, temperatures as high as 750 °C are needed. Difficulty in achieving a low resistivity at low temperature with the TiCl<sub>4</sub> + NH<sub>3</sub> chemistry is attributed to high levels of chlorine impurity being incorporated into the TiN film. The chlorine not only affects the film resistivity but, more importantly, may lead to corrosion of the aluminum interconnects, causing reliability problems. Buiting *et al.* showed the one-to-one correlation between the TiN film resistivity and chlorine impurity level [4] (Fig. 9). Figure 10 shows the combined data reported by Buiting and others for impurity levels *vs.* the deposition

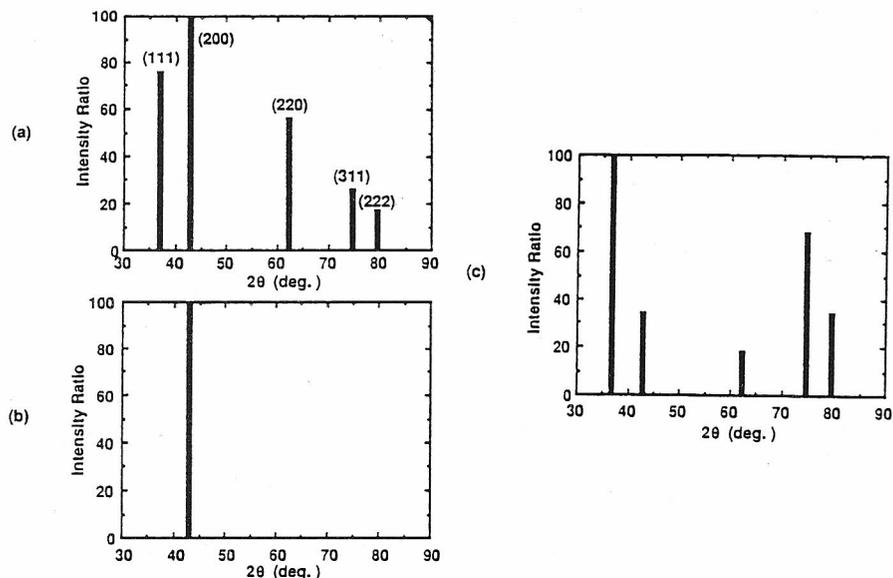


Fig. 5. Preferred orientation of CVD TiN films from  $\text{TiCl}_4 + \text{NH}_3$  by X-ray diffraction: (a) ASTM data; (b) 500 °C deposition; (c) 700 °C deposition [10].

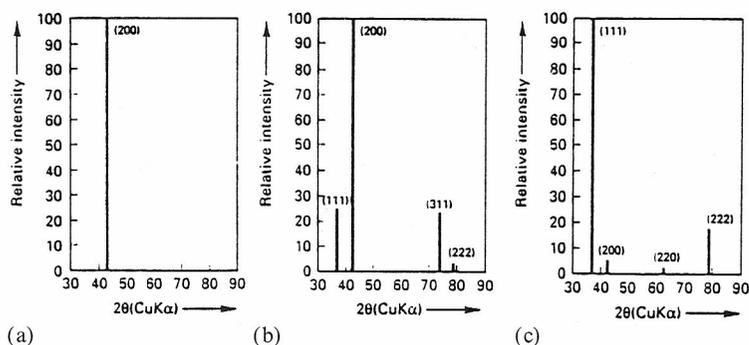


Fig. 6. Preferred orientation of CVD TiN films from  $\text{TiCl}_4 + \text{NH}_3$ , by X-ray diffraction: (a) 0.7–2.3 mTorr; (b) 0.47 Torr; (c) 0.12 Torr [11].

temperature [4, 9, 10, 14]. Sherman also reported lower film resistivities and chlorine impurity levels at lower deposition pressures (100 mTorr *vs.* 300 mTorr) [14]. Another phenomenon observed was increased oxygen and hydrogen impurity levels at higher deposition temperatures, also shown in Fig. 10. The significance of these oxygen and hydrogen impurities was not made evident.

Based on the available data, an acceptable film can be deposited with  $\text{TiCl}_4 + \text{NH}_3$ , but only at high deposition temperatures. As a result, attention has been focused on alternative chemistries for CVD TiN at lower deposition temperatures, using metallo-organic CVD (MOCVD) sources to address the need for compatibility with aluminum.

## 2.2. $\text{TiCl}_4 + \text{MH}$ or TBA

A new focus on alternative CVD chemistries is evolving to reduce the deposition temperature to below

500 °C, while still maintaining optimum film properties. One such example was reported by Suzuki *et al.* using  $\text{TiCl}_4 + (\text{CH}_3)_2\text{NHNH}_2$  (methylhydrazine, MH) at 450 °C [6]. The deposition rate was more than an order of magnitude higher than that from  $\text{TiCl}_4 + \text{NH}_3$  at 450 °C, and it was independent of the temperature (Fig. 2). This process resulted in the degradation of step coverage to 70%. The dominant crystallographic orientation was  $\langle 200 \rangle$ , as shown in Fig. 11. A low resistivity film was achieved at 500 °C, which was comparable with the resistivity of a film grown from  $\text{TiCl}_4 + \text{NH}_3$  at 700 °C. The corresponding chlorine contents are shown in Fig. 10. They also reported aluminum corrosion when the chlorine level in the TiN film was above  $3 \times 10^{21} \text{ cm}^{-3}$ .

Selbrede [9] deposited TiN films with  $\text{TiCl}_4 + (\text{CH}_3)_3\text{CH}_2\text{N}$  and with  $\text{TiCl}_4 + \text{NH}_3$ . Figure 8 shows the resistivity and Fig. 10 the chlorine and carbon concentrations *vs.* the deposition temperature. For a

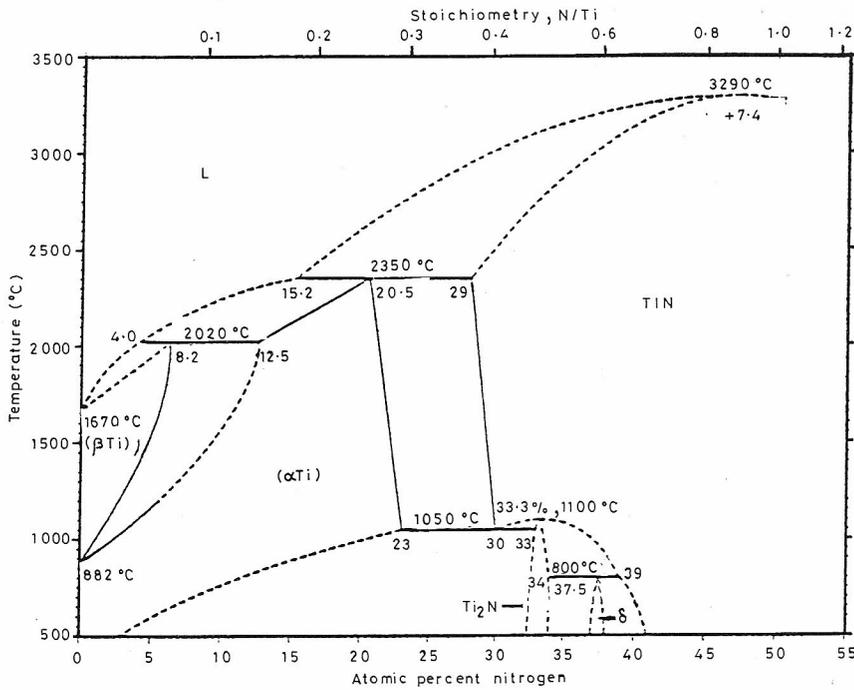


Fig. 7. Ti-N phase diagram [12].

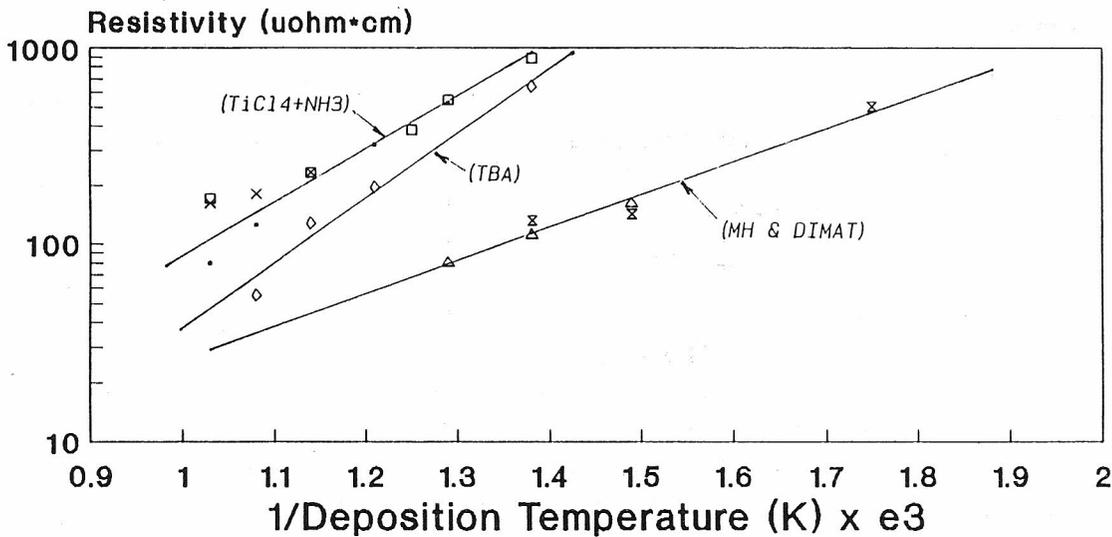


Fig. 8. Graph of film resistivity vs. deposition temperature for four CVD chemistries: ■, Yokoyama et al. [10]; □, Buiting et al. [4]; ×, Genus A; ◇, Selbrede [9]; △, Suzuki et al. [6]; ⊗, Raaijmakers and coworkers [7, 13].

200 μΩ cm film, there were comparable chlorine impurity levels, but the NH<sub>3</sub> chemistry required a deposition temperature more than 100 °C higher to achieve results. Furthermore, a lower minimum resistivity was achieved with the TBA process.

2.3. Tetrakis (DIMAT) + NH<sub>3</sub>

An alternative low temperature CVD TiN chemistry receiving interest is Ti(N(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> (tetrakis dimethyl-

amido-titanium, DIMAT) + NH<sub>3</sub>. Raaijmakers and coworkers reported on this chemistry for TiN films deposited at 10 Torr and temperatures below 450 °C [7, 13]. These films had carbon levels as high as 3 at.% and oxygen of 1 at.% with an N/Ti ratio of 1.22. The step coverage was 30%–60%, depending on the aspect ratio and geometry. This poor step coverage is perhaps because the deposition is gas phase diffusion-limited with an activation energy of 0.09 eV (Fig. 2). Also, the

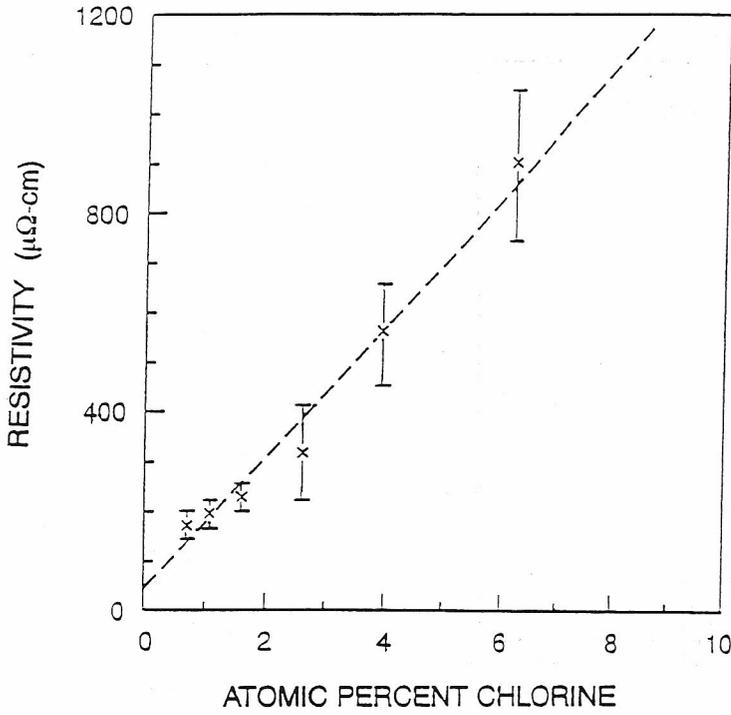


Fig. 9. Graph of CVD TiN film resistivity vs. chlorine concentration [4].

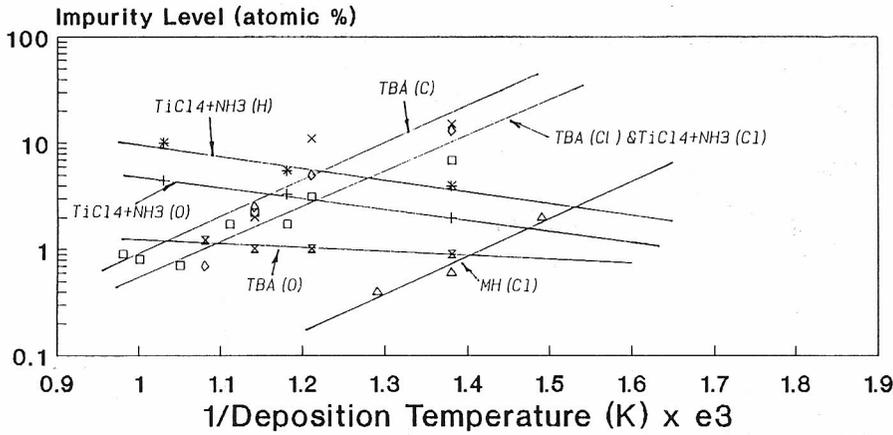


Fig. 10. Graph of grown-in impurity concentrations vs. deposition temperature for several chemistries: +, Sherman [14]; \* Sherman [14]; □, Buiting and Otterloo, [11]; ×, Selbrede [9]; ◇, Selbrede [9]; △, Suzuki et al. [6]; ⌘, Selbrede [9].

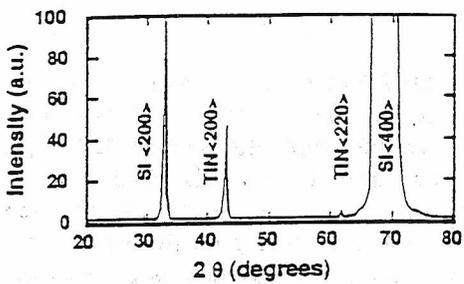


Fig. 11. Preferred orientation of CVD TiN for TiCl<sub>4</sub> + MH, by X-ray diffraction [6].

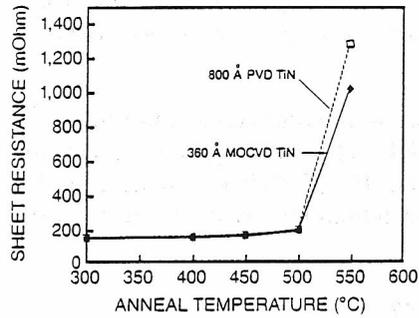


Fig. 12. Barrier performance for DIMAT: sheet resistance vs. annealing temperature [13].

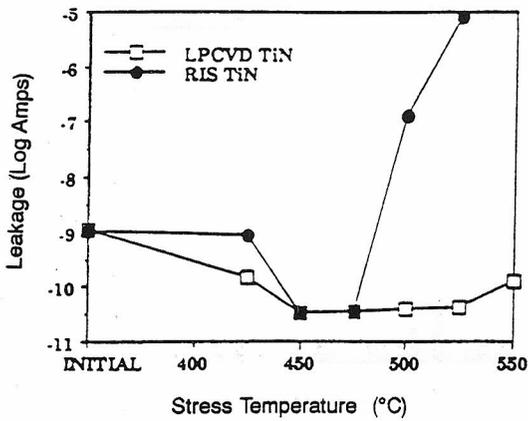


Fig. 13. Barrier performance for  $\text{TiCl}_4 + \text{NH}_3$  vs. sputtered films: junction leakage vs. annealing temperature [15].

microstructure was random, with no columnar grains observed. The resistivity dependence on temperature is shown in Fig. 8, with the resistivity at 450 °C being equivalent to that for films using  $\text{TiCl}_4$  at 625 °C. The diffusion barrier performance and thermal stability up to 500 °C were examined for a Ti/TiN/AlSiCu multilayer structure, as shown in Fig. 12.

### 3. Preclean and device characteristics

Electrical device results for CVD TiN films using  $\text{TiCl}_4 + \text{NH}_3$  were reported by Travis *et al.* [15]. The diode leakage as a function of thermal stressing for CVD and PVD TiN is shown in Fig. 13. The PVD TiN film starts to degrade at temperatures above 475 °C, while no evidence of degradation was observed up to 550 °C with the CVD TiN film. The contact resistance data from Suzuki *et al.* using  $\text{TiCl}_4$  + methylhydrazine for CVD TiN showed tighter distribution than that of PVD TiN on  $p^+$  silicon contacts (Fig. 14) [6]. They also observed tighter diode leakage characteristics (Fig. 15).

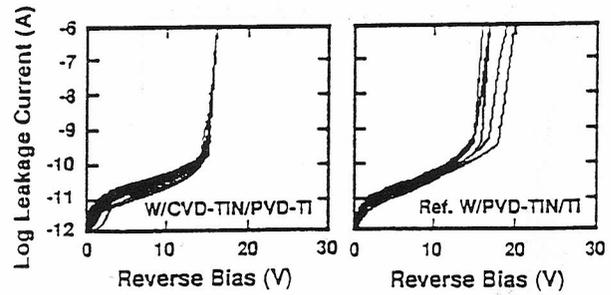


Fig. 15. Junction leakage for 104 parallel contacts of area  $1 \mu\text{m}^2$ : (a) CVD  $\text{TiCl}_4 + \text{MH}$ ; (b) sputtered TiN [6].

Electrical contact resistance measurements are shown in Fig. 16, comparing  $\text{TiCl}_4 + \text{NH}_3$  with DI-MAT +  $\text{NH}_3$ , both with and without an integrated plasma cleaning in a cluster tool. The  $\text{C}_2\text{F}_6 + \text{O}_2$  plasma etch was adjusted to remove 100 Å of thermal oxide. There are two main conclusions.

- (1) Integrated plasma cleaning reduced the contact resistance, regardless of the chemistry.
- (2) With no precleaning, the contact resistance of  $\text{TiCl}_4 + \text{NH}_3$  contacts was lower than that of DI-MAT +  $\text{NH}_3$ . We have theorized that  $\text{TiCl}_4 + \text{NH}_3$  at 700 °C removes most of the native oxide by an as yet unknown mechanism related to temperature.

### 4. Conclusions

- (1) PVD TiN has been the industry workhorse.
- (2) Collimated PVD may be limited to  $\geq 0.35 \mu\text{m}$  device generations.
- (3) CVD TiN using  $\text{TiCl}_4 + \text{NH}_3$  can produce excellent films, with the major trade-off being high deposition temperature and chlorine impurity.
- (4) CVD TiN using MOCVD and  $\text{NH}_3$  has been achieved at low temperature, but suffers from poor step coverage and high resistivity.

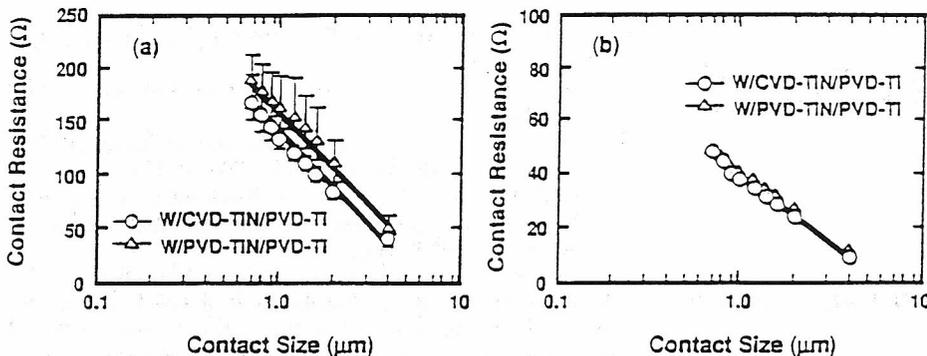


Fig. 14. Contact resistance comparison between sputtered and CVD  $\text{TiCl}_4 + \text{MH}$ : (a)  $p^+$  Si; (b)  $n^+$  Si [6].