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# THERMAL METALORGANIC CHEMICAL VAPOR DEPOSITION OF Ti-Si-N FILMS FOR DIFFUSION BARRIER APPLICATIONS

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## ABSTRACT

Structurally disordered refractory ternary films such as titanium silicon nitride (Ti-Si-N) have potential as advanced diffusion barriers in future ULSI metallization schemes. Here we present results on purely thermal metalorganic chemical vapor deposition (CVD) of Ti-Si-N. At temperatures between 300 and 450°C, tetrakis(diethylamido)titanium (TDEAT), silane, and ammonia react to grow Ti-Si-N films with Si contents of 0-20 at.%. Typical impurity contents are 5-10 at.%H and 0.5 to 1.5 at.% C, with no O or other impurities detected in the bulk of the film. Although the film resistivity increases with increasing Si content, it remains below 1000 μΩ-cm for films with less than 5 at.% Si. These films are promising candidates for advanced diffusion barriers.

## INTRODUCTION

As critical dimensions for ULSI devices continue to shrink, new metallization technologies will be required. One necessity is a conformal, 10-20 nm thick diffusion barrier which is compatible with novel metals such as hot-sputtered Al, CVD Al, or Cu. Presently, sputtered TiN is the standard diffusion barrier, but the poor conformality of sputtering has led to investigations of CVD TiN diffusion barriers. Two primary chemistries have been investigated, using either $TiCl_4$ and $NH_3$ [1], or a Ti metalorganic precursor such as TDEAT (or the similar dimethylamido compound TDMAT) alone or with $NH_3$ [2-4]. It is reportedly difficult, however, to produce TiN films from these metalorganic precursors with low resistivity, good conformality, and low impurity levels. Furthermore, since these TiN films are generally polycrystalline, grain-boundary diffusion will remain as a failure mechanism.

Structurally disordered refractory ternary films such as Ti-Si-N have been shown to be promising candidates for ≈10 nm diffusion barrier applications by experiments on sputtered ternary films [5,6]. Sputtered Ti-Si-N films are thought to be composed of nanocrystals of TiN in a $Si_3N_4$ matrix, giving a barrier with pre-stuffed grain boundaries.

In this paper we report on the development of a CVD process for Ti-Si-N. The process uses TDEAT, $SiH_4$, and $NH_3$ at temperatures from 300 to 450°C. The film resistivity and conformality suggest that these films are attractive candidates for future ULSI diffusion barrier applications.

## EXPERIMENT

The Ti-Si-N films were deposited on 150 mm Si wafers in a Materials Research Corporation Phoenix CVD system. Silane, ammonia, and nitrogen were mixed in the showerhead and flowed down over the wafer, which is mounted on a rotatable, heated susceptor. The TDEAT was in a heated bubbler (normally 80°C) and delivered seperately into the chamber to avoid pre-reactions in the showerhead. Typical precursor flow rates were 100 sccm of $N_2$ as the carrier gas (yielding ~5 sccm TDEAT) in the bubbler, 1000 sccm $NH_3$, 1000 sccm $N_2$, and <1 sccm $SiH_4$. During all depositions the system pressure was maintained at 20 Torr and the wafers were rotated at 100 rpm. The deposition time was varied from 1 to 15 minutes, with 5-10 minutes being typical deposition times for the ~50 nm thick films deposited for analysis. Thermal contact between the susceptor and wafer was enhanced by 10 Torr of He on the backside of the wafer, and the susceptor was kept at temperatures from 300 to 450°C.

Depositions were performed on both thermal oxide and bulk Si wafers, as well as various test structures. Film compositions were measured by Rutherford backscattering spectrometry (RBS) with 3.5 MeV $He^+$ and elastic recoil detection (ERD) using 28 MeV $Si^{5+}$. The films were also characterized by mass gain and resistivity. Gap fill and microstructure were investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

## RESULTS AND DISCUSSION

Figure 1 shows the Si content of films deposited under different precursor flows. It is surprising that $SiH_4$ reacts at all at these temperatures. (Note that $Si_3N_4$ cannot be deposited thermally from $SiH_4$ and $NH_3$ at these temperatures.) As the ratio of $SiH_4$ to TDEAT increases, the amount of Si incorporated in the film increases logarithmically. The TDEAT flow rate was calculated assuming a 1 Torr vapor pressure in the bubbler at 80°C. In addition, higher deposition temperatures result in more Si being incorporated under similar precursor flows. Because all depositions were carried out at a constant pressure (20 Torr), the total gas flow ([All] in the figure) during the deposition determines the average residence time in the reactor, which in turn affects the Si incorporation. As the residence time increases (total flow

decreases), more Si is incorporated in the film at a given $SiH_4$ to TDEAT ratio. The line in Fig. 1 is an extrapolation of the lower $SiH_4$ flow data, and is meant solely to guide the eye. Because $SiH_4$ will neither thermally decompose by itself or react with $NH_3$ at these temperatures, it is clear that there will be an upper limit to the Si content that can be incorporated in a Ti-Si-N film.

Figure 2 shows a Ti-Si-N ternary phase diagram of the films grown using TDEAT, $SiH_4$, $NH_3$, and $N_2$. The tie lines shown are based on the available data from temperatures above 500°C [7], and do not reflect the wide variations possible in N content for the TiN phase. These films are all clustered on the N-rich side of the $Si_3N_4$-TiN tie line. These compositions are encouraging since the most promising sputtered barriers also lie along the $Si_3N_4$-TiN tie line [6]. The only impurities found in the films by RBS or ERD were hydrogen and carbon. Some surface oxygen could occasionally be detected, but, unless the deposition chemistry was too lean in $NH_3$, no O was detected in the bulk of the film.

The resistivity of the film varies dramatically with the Si content, as shown in Fig. 3. Increasing the Si content exponentially increases the resistivity. At Si concentrations below 5 at.%, the film resistivity falls below 1000 μΩ-cm. Different deposition temperatures generate slightly different curves, with the minimum resistivity at a given Si content occuring for deposition temperatures of 350°C. At temperatures above or below 350°C, the films are richer in nitrogen and also have higher resistivities.

The step coverage of these films is very good, which is necessary for conformal coverage of high aspect ratio structures. Figure 4 shows a cross-section SEM of a 50 nm thick $Ti_{0.46}Si_{0.03}N_{0.51}$ film grown at 350°C, which has a resistivity of under 700 μΩ-cm. The film is deposited over 0.5 μm trenches with an aspect ratio of 1.6 through oxide to polysilicon. The step coverage is at least 80%, and the film faithfully reproduces the irregularities on the original structures.

## CONCLUSIONS

We have demonstrated that purely thermal metalorganic chemical vapor deposition can produce Ti-Si-N films with low impurity contents over a wide process window. The precursors, TDEAT, $SiH_4$, and $NH_3$, are readily available and generally accepted. The incorporation of Si can easily be varied across a wide range (0-20 at.%) by changing the ratios of the precursors. Although the film resistivity increases dramatically with Si content, resistivities below 1000μΩ-cm, required for diffusion barrier use, are obtained for Si contents below 5 at.%. Films with these low silicon contents exhibit step coverages of at least 80%

over 0.5 μm trenches with aspect ratios of 1.6. It appears that CVD Ti-Si-N films may be excellent candidates for future ULSI diffusion barriers.

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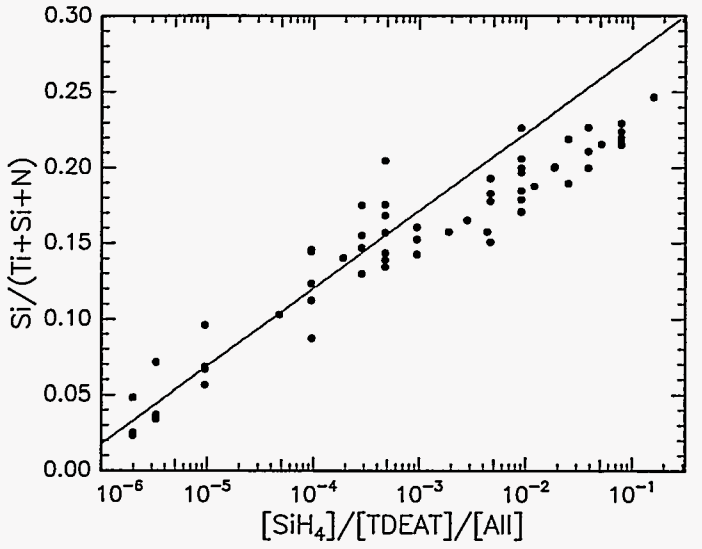


**Figure 1.** The relative Si content of films (ignoring H and C) is shown plotted versus the gas flow conditions during the deposition. As the ratio of $SiH_4$ to TDEAT is increased, the Si content of the film increases logarithmically. All depositions were performed at constant pressure (20 Torr), so the total gas flow ([All]) establishes the residence time in the system. The line is to guide the eye.

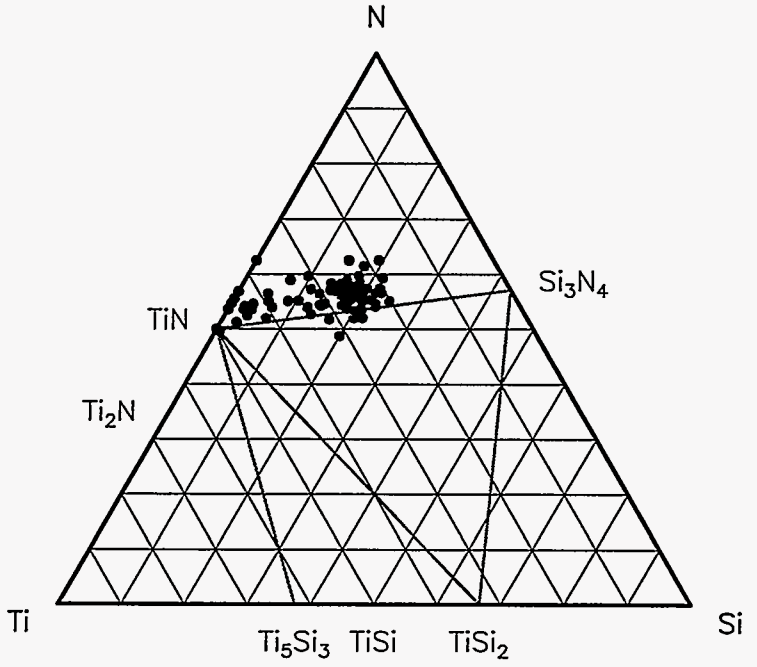


**Figure 2.** Ternary phase diagram of films produced with the TDEAT/$SiH_4$/$NH_3$ process at temperatures from 300 to 450°C. The placement of the points on the phase diagram was determined from the ratios of Ti, Si, and N only; the H and C contents were ignored. Films deposited at 350°C are closest to the tie line, while films at lower and higher temperatures are more N rich.

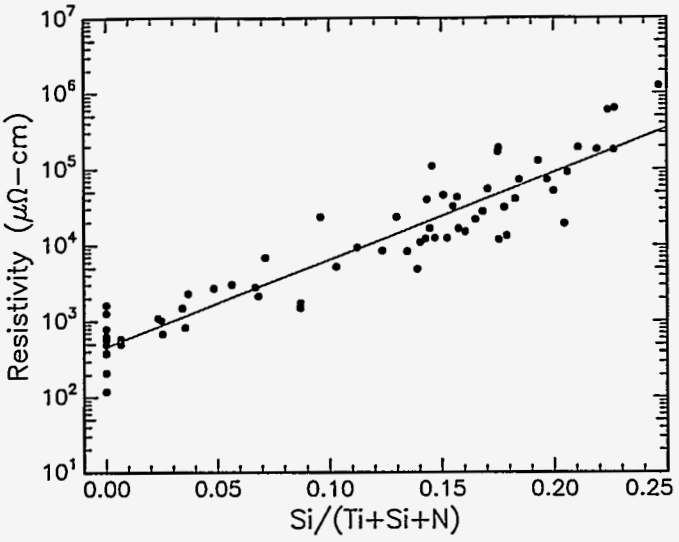


**Figure 3.** Film resistivity is shown versus the Si content in the film for films grown at temperatures from 300 to 450°C. With increasing Si content, the resistivity increases exponentially. Film resistivities below 1000μΩ-cm are can be obtained for films with less than 5 at.% Si. Films grown at 350°C have the lowest resistivity at a given Si content. The line is to guide the eye.

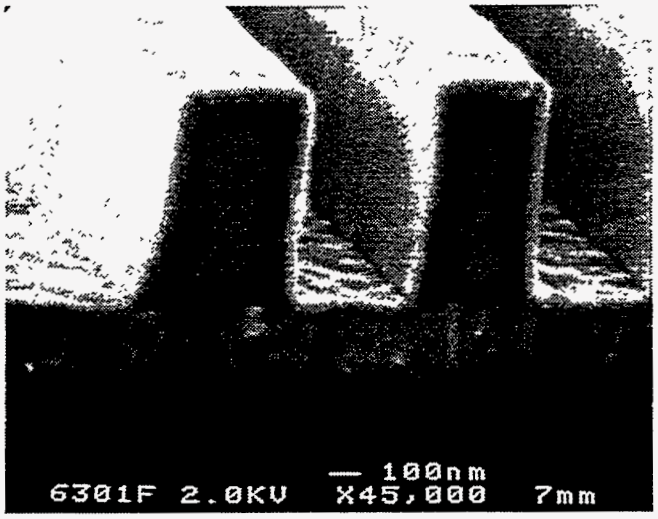


**Figure 4.** A cross-section SEM of a 50 nm thick $Ti_{46}Si_{03}N_{51}$ film grown at 350°C, which has a resistivity of under 700μΩ-cm. The film is deposited over 0.5μm lines with an aspect ratio of 1.6 through oxide to polysilicon. The step coverage is at least 80%, and the film faithfully reproduces the irregularities on the original structures.