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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. We demonstrate chemical vapor deposition (CVD) of Ti-Si-N-containing films in a commercially available single-wafer CVD system using two different Ti precursors, $TiCl_4$ and tetrakis(diethylamino)titanium (TDEAT). In particular, the TDEAT-based films can be grown conformally with low impurity content, and are promising candidates for advanced diffusion barrier applications.

Introduction

As critical dimensions for ULSI devices shrink ever smaller, 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 accepted material for diffusion barrier applications. The poor conformality of sputtering techniques has led to investigations of CVD TiN diffusion barriers, with two primary chemistries emerging as very promising. The first uses $TiCl_4$ and NH_3, and produces TiN films containing some Cl, which is problematic because of the corrosion problems associated with Cl [1-3]. The second CVD chemistry uses metalorganic precursors such as tetrakis(dimethylamino)titanium (TDMAT) or tetrakis(diethylamino)titanium (TDEAT) in combination with NH_3. It is reportedly difficult, however, to produce TiN films from these metalorganic precursors with low resistivity, good conformality, and low impurity levels [4,5]. Furthermore, since these TiN films are polycrystalline their barrier properties may be inadequate because of grain-boundary diffusion, particularly at thicknesses below 20 nm.

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 [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[6-8]. Industrially relavent techniques for CVD of Ti containing ternaries, however, are relatively limited to date. Eizenberg *et al.* reported on the deposition of Ti-C-N from TDMAT and NH_3 [5], indicating that the films were deposited conformally and were effective diffusion barriers. Raaijmakers *et al.* briefly reported on the deposition of Ti-Si-N from TDEAT, SiH_4, and NH_3 in 1994 [9], while Doan and Sandhu have patented a CVD technique using metalorganic precursors like TDEAT, along with SiH_4 and NH_3 for the deposition of films containing both TiN and $TiSi_2$ [10]. Li *et al.* have also reported on a plasma enhanced CVD process for the deposition of Ti-Si-N at 560°C [11].

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In this letter we report on the development of two CVD processes for Ti-Si-N. The first uses $TiCl_4$, Si_2H_6, and NH_3 at temperatures of at least 500°C. The relatively high deposition temperature, potential impact of chlorine in the films, and safety issues regarding Si_2H_6 make this film unattractive for commercial integrated circuit applications. The second process uses TDEAT, SiH_4, and NH_3 at 300 to 450°C. The conformality of the deposited material and preliminary electrical measurements indicate these films are attractive diffusion barrier candidates for ULSI applications.

Procedure

The Ti-Si-N films were deposited on 150 mm Si wafers in a Materials Research Corporation Phoenix CVD system. The precursors are mixed in the showerhead, except where noted otherwise, and flow down over the wafer, which is mounted on a rotatable, heated susceptor. 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 4 minutes being the typical deposition time. Thermal contact between the susceptor and wafer was enhanced by 10 Torr of He on the backside of the wafer. 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. Microstructure and gap fill were investigated with scanning electron microscopy (SEM). Film crystallinity was characterized by Read camera x-ray diffraction. Biased-thermal-stress testing of MOS capacitors was performed to test the effectiveness of the films as diffusion barriers for Cu metallization. The CVD films were compared against a sputtered TiN film produced by reactive DC magnetron sputtering of a Ti target in a N_2/Ar plasma in a system with a base pressure of 2×10^{-7} Torr.

One chemistry investigated was $TiCl_4$, Si_2H_6, and NH_3 at a deposition temperature of 500°C. Precursor flow rates were in the range of 0-50 sccm $TiCl_4$, 0-100 sccm NH_3, and 0-250 sccm Si_2H_6, with 5000 sccm N_2 to establish the overall flow pattern in the reactor. The use of Si_2H_6 rather than SiH_4 was required to obtain Si in the films at this temperature. The second chemistry used TDEAT, SiH_4, and NH_3 at deposition temperatures from 300-450°C. It is surprising that the SiH_4 reacted at these low temperatures; as shown in Table I, given the temperature required for SiH_4 to react with NH3. This indicates that incorporation of Si in the films must somehow be promoted or catalyzed by the breakdown of TDEAT. The TDEAT was delivered from a heated bubbler (normally 80°C) using 25-200 sccm of N_2 as carrier gas. The other precursor flow rates were 0-2000 sccm NH_3, 0-2000 sccm N_2, and 0-500 sccm SiH_4. Unfortunately, TDEAT reacts with the other precursors at the temperatures reached inside the showerhead, resulting in poor film quality (high concentrations of C and O). The showerhead assembly was therefore modified to provide an individual injection port for TDEAT. While the films had very low impurity contents, the modified showerhead configuration produced non-uniform depositions that made determination of the film thicknesses and resistivities imprecise.

Results and Discussion

Figure 1 shows a Ti-Si-N ternary phase diagram [13] of the films grown using both the $TiCl_4$ and TDEAT chemistries, including $TiCl_4$-based films with Cl ≤18 at.% and O ≤30 at.% and TDEAT-based films with C ≤3 at.% and O ≤3 at.%. The $TiCl_4$-based film compositions generally follow a line from $TiSi_2$ (grown without NH_3) to TiN (grown without Si_2H_6), while the TDEAT-based films are clustered on the N-rich side of the Si_3N_4-TiN tie line (pure Si_3N_4 cannot be deposited thermally at these temperatures). Raaijmakers *et al.* also found that TiN from TDEAT and NH_3 is N rich [3]. These two chemistries allow access to a large region of the Ti-Si-N phase diagram, although the most promising barriers from previous sputtering studies are most likely along the Si_3N_4-TiN tie line [7]. The only impurities found in the films by RBS or ERD were O, H, and either C (in TDEAT-based films only) or Cl (in $TiCl_4$-based films only). Impurity concentrations in the $TiCl_4$-based films were typically 2-10 at.% Cl, 2-5 at.% H, and up to 30 at.% O in some films. Oxygen was incorporated into these films upon exposure to air, as monitored by color change and mass gain of the wafers over time. Precursor mixes richer in NH_3 resulted in air-stable films with O contents below the detection limit of $\approx$1 at.%, although these conditions also limit the Si incorporation. TDEAT-based films contained 8-21 at.% H, 1-30 at.% C, and 1-30 at.% O (again entering the film upon exposure to air) as impurities. Both the C and O contents could be reduced to below 3 at.% by using sufficient NH_3 flows, producing air-stable films.

Figure 2 shows cross-sectional SEMs of a $TiCl_4$-based film and a TDEAT-based film deposited over an oxide step structure. The $TiCl_4$-based film [Figure 2(a)] (deposited at 500°C with 20 sccm $TiCl_4$, 500 sccm Si_2H_6, and 20 sccm NH_3) exhibits a thin, conformal layer, covered by a layer that contains dendritic-like fiber bundles. Stopping the depositions before the fibrous material forms might produce films that are suitable for microelectronic applications, although it was not determined if these two regions have differing compositions. The very rough film cross section also makes it impossible to determine the resistivity. In contrast, the TDEAT-based film [Figure 2(b)] (deposited at 350°C with 100 sccm TDEAT carrier gas (N_2), 100 sccm SiH_4, and 1000 sccm NH_3) grows conformally over the oxide steps at a rate of 10-20 nm/minute, with step coverage of better than 80%. The vertical structure seen in the Ti-Si-N film is also observed on the original oxide steps and is a result of the etch used to define the structures. This conformality is similar to that observed previously for optimized TDEAT-based TiN films (85% on similar structures) [9]. The resistivity of the TDEAT-based films as a function of Si content is shown in Figure 3. As the Si content rises, there is a strong increase in resistivity from $\approx$200 $\mu\Omega$-cm for pure TiN films to over 1 Ω-cm at 25 at.% Si. The deposited films may be in the free nitrogen regime, based on equilibrium thermodynamics, and weakly bonded N will tend to increase the resistivity of the films. From this data we believe that we can grow films with resistivities of $\leq$1000 $\mu\Omega$-cm by lowering the Si and/or N content. The gap in the data from 0 at.% Si to $\approx$12 at.% Si represents a SiH_4 flow regime that was inaccessable with the mass flow controller used for this study.

Precursors	Minimum Deposition Temperature	Deposited Material
TDEAT/SiH_4/NH_3	300°C	Ti-Si-N
TDEAT/NH_3	280°C [3]	TiN
TDEAT/SiH_4	450°C [9]	Undetermined
SiH_4/NH_3	700°C [12]	Si_3N_4

Table I. Precursor combinations for the TDEAT/SiH_4/NH_3 deposition chemistry, minimum temperature required to obtain thermal CVD from these precursors, and constituents in the deposited material.

Films produced using both the $TiCl_4$ and TDEAT chemistries were investigated using x-ray diffraction. TiN films from these precursors are polycrystalline, as has been observed previously [2,14]. In contrast, as-deposited Ti-Si-N films appear to be structurally disordered with a nanophase TiN component from the Read camera data. A 900°C anneal of the Ti-Si-N films for 1 hour produced material that contained polycrystalline TiN, by x-ray diffraction. We are reluctant to identify the as-deposited films as amorphous, since high-resolution TEM studies on sputtered Ti-Si-N have shown nanocrystalline TiN surrounded by an amorphous matrix (probably Si_3N_4) when the x-ray data indicated an amorphous film [7,8]. The resistivity data in Figure 3 suggests that the CVD Ti-Si-N films have a similar microstructure, as increasing Si content (possibly as Si_3N_4) rapidly increases the resistivity, as might happen if conduction were by hopping, or tunneling, between TiN nanocrystals. Certainly, the Ti-Si-N films do not contain large grains, allowing very thin films to be deposited uniformly, which is necessary for thin diffusion barrier applications.

To evaluate the potential of the TDEAT-based films as diffusion barriers, biased-thermal-stress testing of MOS capacitors with Cu metallization over nominally 10 nm thick diffusion barriers was performed. The capacitors were stressed with 50 V at 200°C, and the leakage current through the 100 nm oxide was monitored. When the diffusion barrier failed, Cu diffused rapidly through the oxide and caused oxide breakdown, leading to a rapid increase in the leakage current from approximately 1 nA/cm^2 to approximately 10 mA/cm^2. Figure 4 shows failure data versus the inverse of the standard normal cumulative distribution for a sputtered TiN film, a TDEAT-based film deposited at 350°C (with a composition of $Ti_{0.31}Si_{0.09}N_{0.47}C_{0.01}H_{0.12}$), and a TDEAT-based film deposited at 400°C ($Ti_{0.23}Si_{0.14}N_{0.45}O_{0.03}C_{0.03}H_{0.12}$). The 400°C TDEAT-based film has a mean time to failure that is almost a factor of 100 larger than that measured for the sputtered TiN. These preliminary results indicate that the CVD Ti-Si-N films, especially the TDEAT-based films, may be suitable for diffusion barrier applications in ULSI devices.

Conclusion

Two CVD processes for structurally disordered refractory ternary Ti-Si-N have been developed in a commercially available cluster tool. The first process combines $TiCl_4$, NH_3, and Si_2H_6 at deposition temperatures of at least 500°C, while the second uses TDEAT, NH_3, and SiH_4 at temperatures of 300-450°C. Of these, the TDEAT process is more promising because of the precursors used, the lower deposition temperature required, and the conformal films produced. The two chemistries cover a wide range of the ternary phase diagram, including compositions near the TiN-Si_3N_4 tie-line which are preferred for diffusion barriers [7]. Both chemistries result in Ti-Si-N films that appear to be structurally disordered by x-ray diffraction. The TDEAT-based films have deposition rates and conformality sufficient for thin barrier applications, and we believe that film resistivities of less than 1000 $\mu\Omega$-cm can be produced. The initial biased-thermal-stress data indicate that the TDEAT-based films are better than sputtered TiN as diffusion barriers for Cu metallization. Although further work is needed to improve film uniformity, optimize the barrier properties, and address integration issues, we believe this work marks a major step forward in the development of advanced CVD diffusion barrier processes for future ULSI applications.

Acknowledgments

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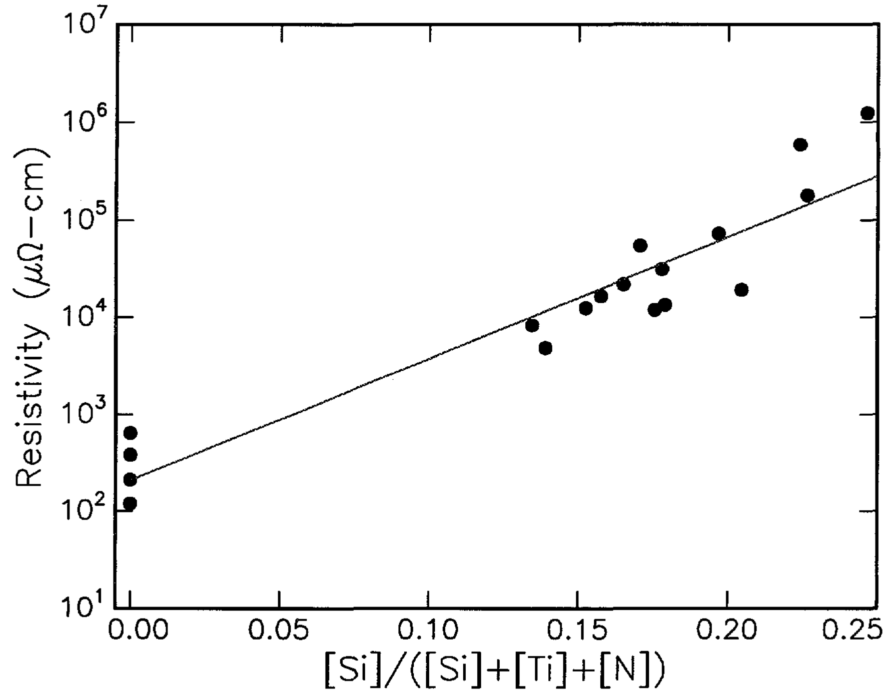


Figure 3. Resistivity of the TDEAT films as a function of Si content. There is a very strong increase in resistivity with Si content. The gap in the data from 0 to ≈12 at.% Si represents a SiH_4 flow regime that could not be accessed by the mass flow controller used in this study.

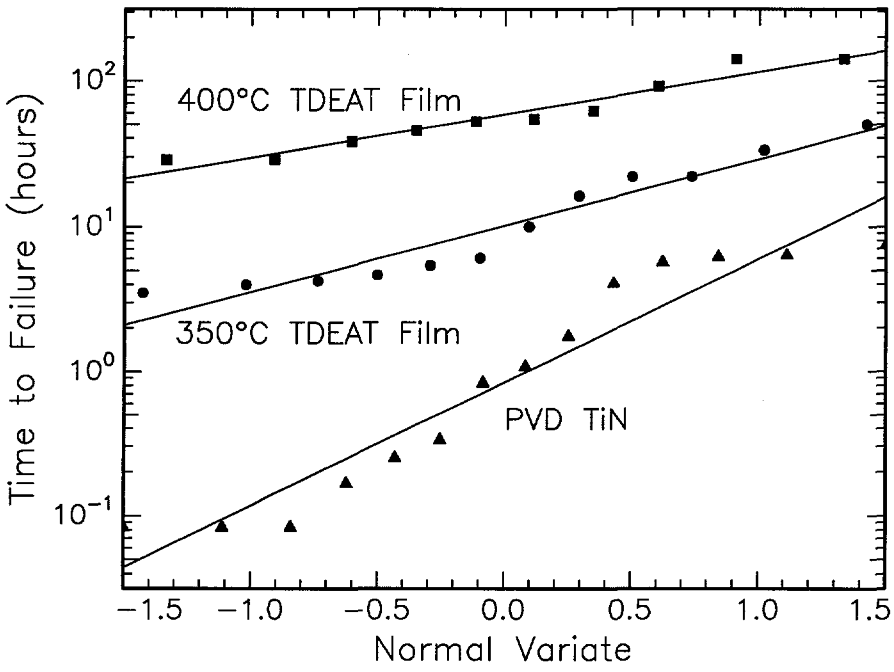


Figure 4. Biased-thermal-stress failure data for a sputtered TiN film and two TDEAT-based films, one deposited at 350°C, and the other at 400°C. The diffusion barrier thickness in all cases is nominally 10 nm. The 400°C TDEAT-based film has a mean time to failure that is almost 2 orders of magnitude larger than that of the TiN film.

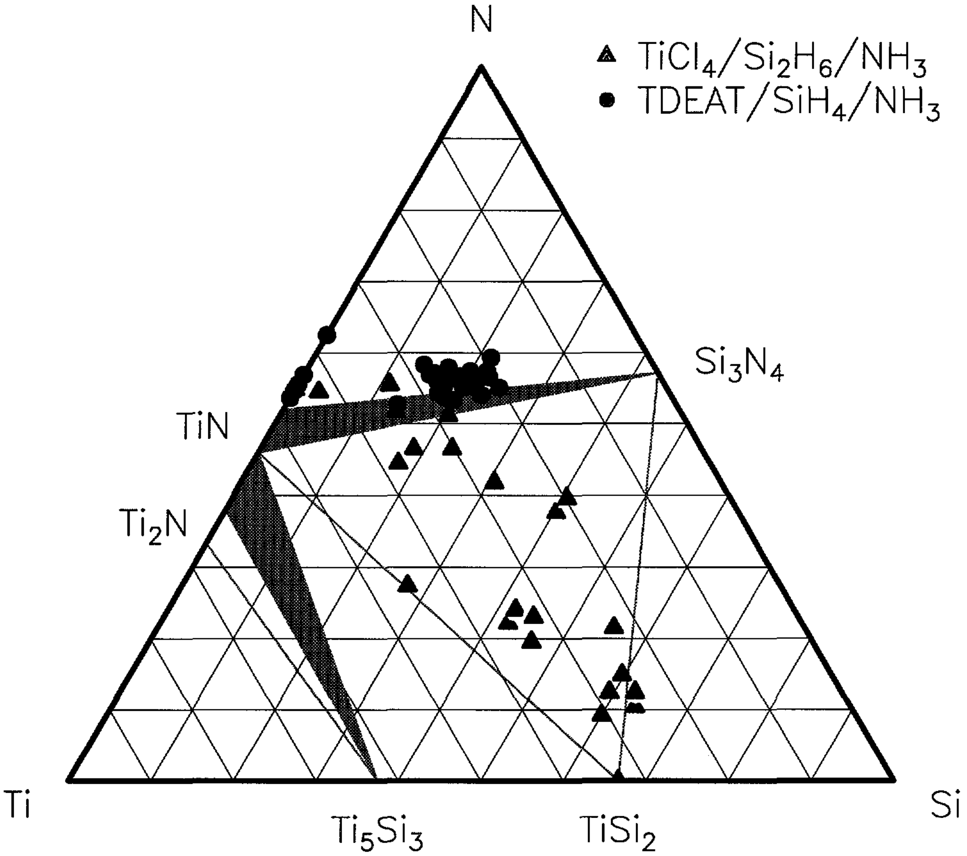
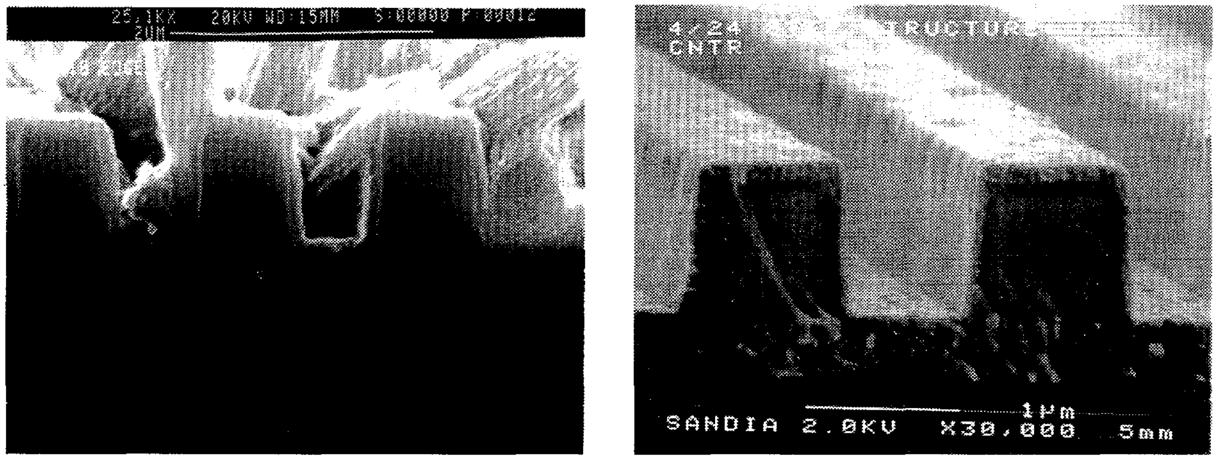


Figure 1. Ternary phase diagram of films produced with the $TDEAT/SiH_4/NH_3$ and $TiCl_4/Si_2H_6/NH_3$ CVD processes. The film stoichiometries are determined from the ratios of Ti:Si:N, ignoring any incorporated impurities. A wide stoichiometric range is accessed by use of the two chemistries reported here.



A

B

Figure 2. Cross-sectional SEMs of a $TiCl_4$-based film (a) and a TDEAT-based film (b) deposited over an oxide step structure. The $TiCl_4$-based film is composed of a thin, conformal layer and a layer made up of dendritic-like fiber bundles. It was not determined if the two growth regimes have the same composition. The TDEAT-based film is seen to be very conformal and to have step coverage of better than 80%.