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CHEMICAL VAPOR DEPOSITION OF TERNARY REFRACTORY NITRIDES FOR DIFFUSION BARRIER APPLICATIONS

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ABSTRACT

As semiconductor device dimensions shrink, new diffusion barriers will be required. Amorphous refractory ternaries have been identified as promising barrier candidates based on experiments on sputtered films. Because sputtering may not meet future requirements we have developed chemical vapor deposition processes for these materials. Acceptable deposition rates are found for each of these processes at 350°C, with all depositions performed between 300 and 450°C. The first process produces a range of Ti-Si-N compositions from TDEAT, SiH_4, and NH_3. The resistivity of the Ti-Si-N films decreases with decreasing Si content from over 1 Ω-cm at ≈25 at. % Si down to that of TiN (≈200 μΩ-cm). The step coverage obtained is better than 80% on 0.5 μm features with aspect ratios of >1.6. The second CVD process produces a range of W-Si-N film compositions from WF_6, Si_2H_6, and NH_3. The resistivities vary with composition from 350 to 20,000 μΩ-cm. The step coverage obtained is 100% on reentrant 0.25 μm features with aspect ratios of 4.0. The third CVD process employs WF_6 (reduced by SiH_4), B_2H_6, and NH_3 to produce W-B-N films with a range of compositions. Resistivities range from 200 to 20,000 μΩ-cm. The step coverage obtained is ≈40% on 1.5 μm features with aspect ratios of 5.5.

INTRODUCTION

There is currently great interest in the chemical vapor deposition (CVD) of diffusion barriers for both aluminum and future copper metallization schemes. It has been demonstrated that thin ternary refractory-based films are excellent diffusion barriers to both copper and aluminum [1-10]. These materials have typically been deposited by physical deposition, or sputtering, and it is not expected that this deposition technique can be used to deposit films with adequate conformality and barrier properties under the stringent requirements currently envisioned for 0.18 μm technologies and beyond. Films deposited by CVD can exhibit superior step coverage compared with sputtered films and the properties of the deposited films are often similar. In this work we have used CVD processing to grow three distinct ternary refractory nitride films: Ti-Si-N, W-Si-N, and W-B-N. The precursors used in this work are widely available and generally accepted by the semiconductor industry.

EXPERIMENTAL PROCEDURE

All of the depositions reported here were performed on 150 mm Si wafers. Depositions were conducted on bare silicon, oxide coated wafers, or on patterned test structures. All of the depositions were performed between 300 and 450°C, with the typical deposition temperature being 350°C. The resulting film compositions were measured by Rutherford backscattering spectrometry (RBS) with 3.5 MeV He^+ and elastic recoil detection (ERD) using 28 MeV Si^{5+}. Surface morphology, gap fill, and film thickness were observed by SEM, and sheet resistivity was determined by four point probe.

The deposition system used for the titanium based films is a Materials Research Corporation Phoenix CVD cluster system consisting of a cassette loadlock, a Brookes cluster hub, and a CVD chamber. The wafer is mounted on a rotatable, heated susceptor.

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Thermal contact between the susceptor and wafer is enhanced by 10 Torr of He on the backside of the wafer.

The precursors used to produce the Ti-Si-N films are SiH_4, NH_3, and $Ti(N(C_2H_5)_2)_4$ (tetrakis(diethylamido)titanium, or TDEAT) delivered from an 80°C bubbler by up to 200 sccm of N_2. The precursor flow rates are typically 100 sccm N_2 carrier gas (yielding $\approx$5 sccm TDEAT), 1000 sccm NH_3, 1000 sccm N_2, and <1 sccm SiH_4. The TDEAT flow rate was calculated assuming a 1 Torr vapor pressure in the bubbler at 80°C. The precursors, except for the TDEAT, mix in the showerhead prior to introduction into the reaction chamber. The showerhead is actively cooled, but reaches elevated temperatures because it is in close proximity to the susceptor. Because TDEAT reacts with the other precursors in the warm showerhead, it was modified to allow injection of the TDEAT separately. During all of the Ti-Si-N depositions the system pressure was maintained at 20 Torr and the wafers were rotated at 100 rpm. The deposition time was typically 5 to 10 minutes.

The deposition system used for the tungsten based films is a simple cold-wall loadlocked single wafer reactor. The wafers are mounted on a fixed heated susceptor. The gases are distributed through six separate concentric injection rings spaced 4 inches above the surface of the wafer. The precursors were kept separate and allowed to mix only in the low pressure reaction chamber. Argon was used as a carrier/diluent gas. The deposition pressure was typically 500 to 700 mTorr, and the system was evacuated using an oil based mechanical pump.

The W precursor for all of the W containing films is WF_6. For the W-Si-N films, the WF_6 is mixed with a combination of Si_2H_6, NH_3, and Ar. The Ar flow is typically 300 sccm and the WF_6 flow is typically 5 to 20 sccm. The NH_3 and Si_2H_6 flows vary between 10 and 150 sccm. The W-B-N films are produced with WF_6 and a combination of SiH_4, NH_3, 30% B_2H_6 in N_2, and Ar. The Ar, WF_6, and SiH_4 flows are typically 200, 5, and 3 sccm respectively. The NH_3 and B_2H_6 flows vary between 10 and 70 sccm.

RESULTS AND DISCUSSION

Figure 1 shows the film compositions obtained for the Ti-Si-N, W-Si-N, and W-B-N systems. Figure 1(a) shows the Ti-Si-N ternary phase diagram of the films grown using TDEAT, SiH_4, and NH_3. The tie lines shown are based on the available data from temperatures above 500°C [11], 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 [10]. The only impurities found in the Ti-Si-N films by RBS or ERD were H and C, typically 5 to 10 at. % and <1.5 at. %, respectively. Some surface O is occasionally detected, but, unless the deposition chemistry is too lean in NH_3, no O is detected in the bulk of the film.

It is surprising that Si is incorporated into the Ti-Si-N films 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. In addition, higher deposition temperatures result in more Si being incorporated under similar precursor flows. Also, as the residence time in the reactor increases more Si is incorporated into the films at a given SiH_4 to TDEAT ratio. 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 the Ti-Si-N films.

The resistivities of the Ti-Si-N films vary dramatically with Si content, as shown in Figure 2. 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 resistivity curves, with the minimum resistivity at a given Si content occurring 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 good, as measured on a 50 nm thick $Ti_{0.46}Si_{0.03}N_{0.51}$ film grown at 350°C with a resistivity under 700 μΩ-cm. Cross-sectional SEM indicates the step coverage for this film is greater than 80% over 0.5 μm oxide lines on polysilicon with aspect ratio >1.6. The Ti-Si-N films have deposition rates that typically range from 10 to 20 nm/minute.

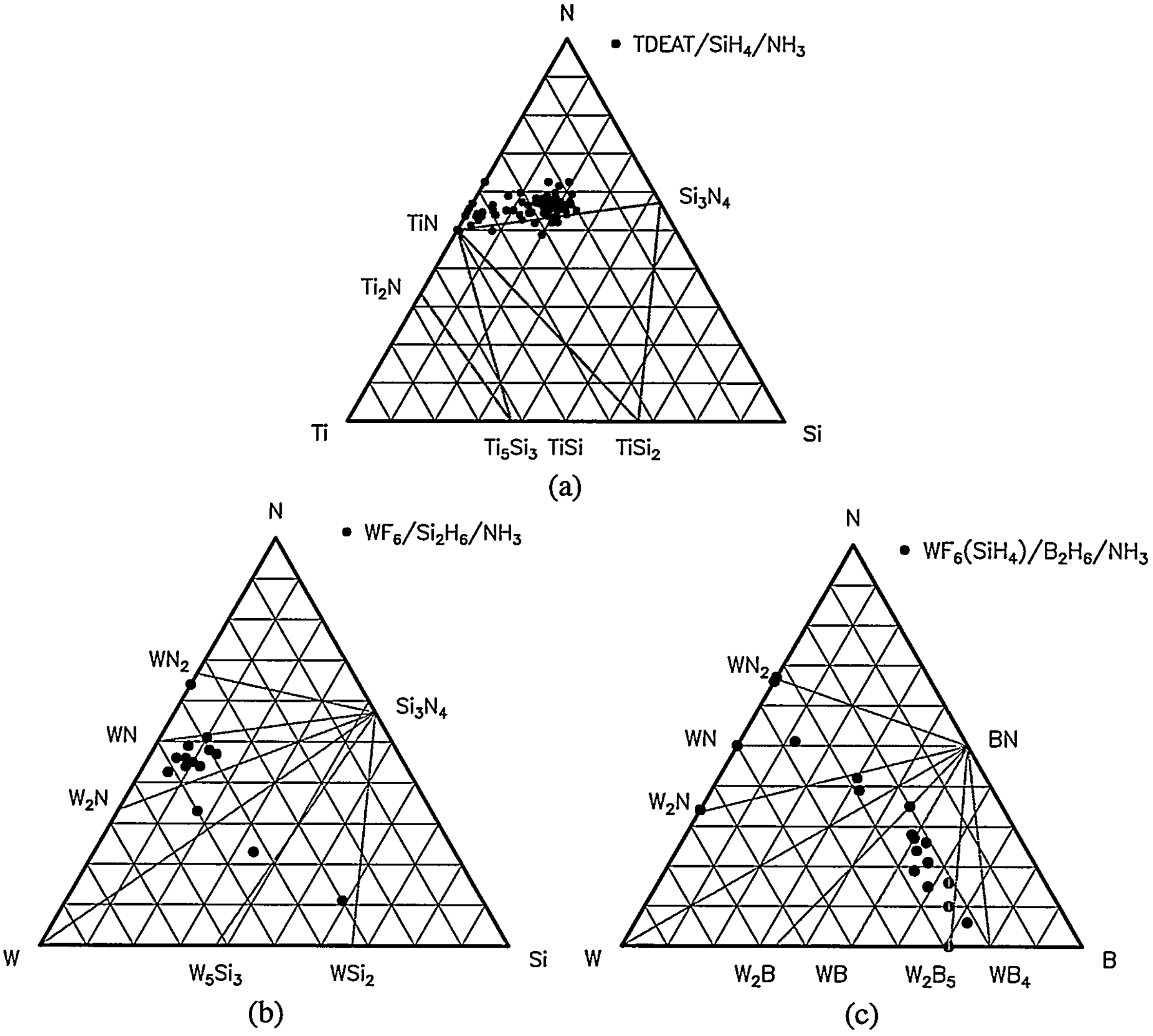

Figure 1. Composition of CVD Ti-Si-N films (a), W-Si-N films (b), and W-B-N films (c).

The W-Si-N compositions grown are indicated on the ternary phase diagram, Figure 1(b). In general, increasing the NH_3 flow reduced the amount of Si incorporated in the film. This effect was complicated, however, by an undesirable side reaction between WF_6 and NH_3 on the cooled showerhead and other parts of the chamber which produces a solid adduct. Because of this side reaction, increasing the WF_6 flow effectively reduced the NH_3 activity over the wafer and the extent of the reaction seemed to depend on the condition of the chamber. This problem can probably be addressed by improving the gas delivery and pumping systems. When the NH_3 flow is sufficiently high, WN_2 is produced. Conversely, if no NH_3 is present, WSi_x is formed. Even though the deposition temperature was relatively low, there was little H incorporation in the films, typically <5 at. %, as determined by ERD.

Tungsten was incorporated into the W-Si-N films through the reduction of WF_6. Thermodynamics predicts that Si_2H_6 is the preferred reductant in the gas mixture and the Si_2H_6 also acts as the source of Si in the films. No Si was incorporated into the films using SiH_4 as a reductant in the presence of significant NH_3 partial pressure and typically produce films with a composition corresponding to WN_2. Nitrogen was incorporated through the reaction of NH_3 with W on the growing surface.

The deposition rates of the W-Si-N films range from 5 to 500 nm per minute, with films deposited from high Si_2H_6 and lean NH_3 mixtures having the highest deposition rates. The as-deposited W-Si-N films have resistivities ranging from 350 μΩ-cm for films close to WN to ≈20 mΩ-cm for WN_2 films. The resistivity appears to be determined by which tie triangle the composition lies in, and on the Si concentration for compositions within that tie triangle. The compositions between 5 and 15 at. % Si lie within the W_2N-WN-Si_3N_4 tie triangle and within this range of compositions the resistivity increases with increasing Si fraction. As the Si fraction is increased further the compositions fall within other tie triangles. For example, with 34 at. % Si the composition moves into the W-Si_3N_4-W_5Si_3 tie triangle and the resistivity falls to well below the value that would be predicted purely from the trend observed between 5 and 15 at. % Si incorporation. This may be due to the presence of the more conductive W and W_5Si_3 phases present in this tie triangle. A similar effect may also occur for the composition with 17 at. % Si which lies within the W_2N-W-Si_3N_4 tie triangle. In cases where an insufficient partial pressure of Si_2H_6 is present, films with compositions corresponding to WN_2 are grown. These films lie outside the W_2N-WN-Si_3N_4 tie triangle and have resistivities of ≈20 mΩ-cm. This increase in resistivity with N content in the WN_x binary is in good agreement with the result of Kattelus, [12] who found a resistivity of 4.5 mΩ-cm for a sputtered film with composition $W_{0.35}N_{0.65}$.

As seen in Figure 3, step coverage of the W-Si-N films is exceptional. The step coverage is 100%, even on extremely aggressive structures with reentrant features and ≈4:1 aspect ratios at 0.25 μm. The film composition in this case is $W_{0.46}Si_{0.08}N_{0.46}$ and the resistivity is 450 μΩ-cm. Since step coverage of aggressive features is one of the major problems with most other diffusion barrier systems, this is an extremely encouraging result. This effect is probably due to adsorption of NH_x fragments on the film surface, lowering the sticking coefficients of the other gas phase components.

The W-B-N film compositions are indicated on the ternary phase diagram, Figure 1(c). Even though the temperature used was relatively low, there was little H incorporation in the films, typically ≈5 at. %, as determined by ERD. In general, increasing the partial pressure of either B_2H_6 or NH_3 increased the fraction of the appropriate element in the film. The deposited ternary compositions lie in a band roughly between 20 and 40 at. % W. Tungsten was incorporated into the films through the reduction of WF_6. Thermodynamics predicts that SiH_4 is the preferred reductant in the gas mixture. The ratio of WF_6 to SiH_4 was greater than 1, and Si incorporation was typically less than 5 at. %. Because B_2H_6 is unstable at room temperature, B was probably incorporated into the films through simple decomposition of B_2H_6, possibly catalyzed by the presence of W. Nitrogen was incorporated through the reaction of NH_3 with W on the hot wafer surface. It was not possible to increase the W fraction in the film by either increasing the WF_6 partial pressure by a factor of eight or by varying the temperature from 200 to 400°C. At the lowest temperature, the deposited films were unstable in air, possibly due to the presence of unreacted B or boron hydrides.

The W-B-N deposition rates range from 50 to 200 nm per minute. The rate increases with lower flows of NH_3 and higher flows of B_2H_6 and SiH_4. Step coverage is ≈40% on

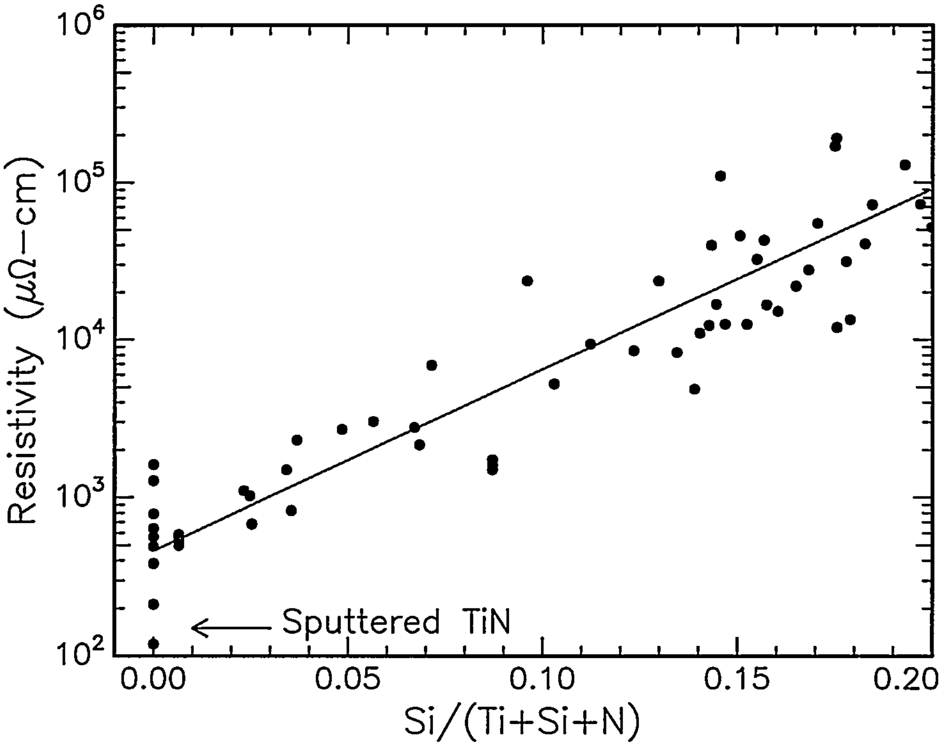

Figure 2. Resistivity versus Si concentration for the Ti-Si-N films. Material was produced with resistivities ranging from that of CVD TiN, (≈200 μΩ-cm) to approximately 1 Ω-cm by varying the amount of incorporated Si.

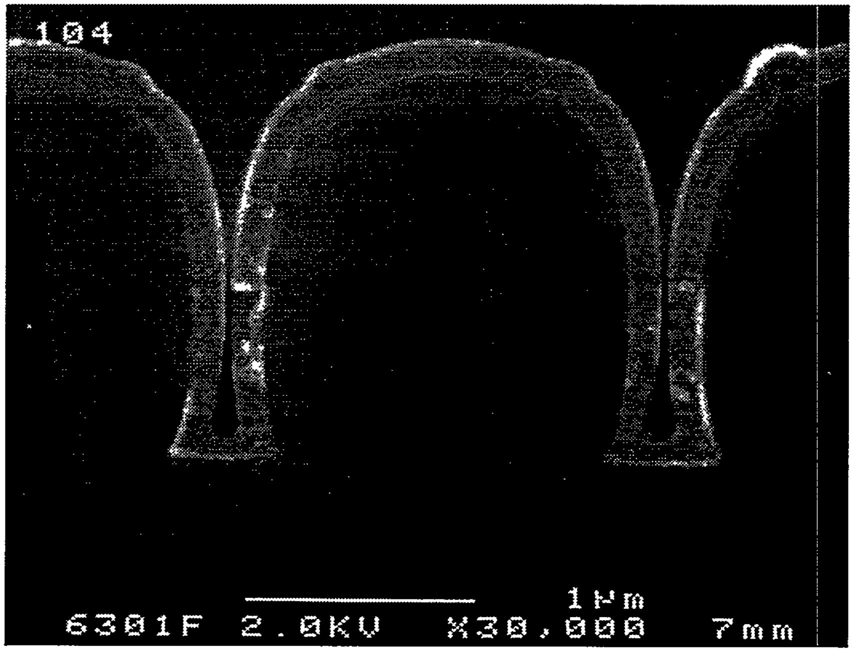

Figure 3. Conformality of $W_{0.46}N_{0.46}Si_{0.08}$ film over 0.25 μm reentrant features with aspect ratio of 4:1. The conformality is 100%, even on these aggressive structures.

samples with aspect ratios of 5.5 and 1.5 μm diameter. The film composition in this case is $W_{0.24}B_{0.66}N_{0.10}$ and the resistivity is approximately 1400 μΩ-cm. The deposition conditions are not yet optimized for step coverage, however, and the very high surface area (≈450 cm^2) of the structure used for this particular test may have degraded the step coverage. The as-deposited films have resistivities ranging from 200 μΩ-cm for WB_x rich films, to ≈20 mΩ-cm for WN_x rich films. In general, ternary films with a higher fraction of WN_x displayed a higher resistivity.

CONCLUSIONS

Thermal CVD of Ti-Si-N, W-Si-N, and W-B-N films has been demonstrated with low impurity content. The precursors are all readily available and generally accepted. The resistivities attainable with each system extend well below 1000 μΩ-cm, which is generally identified as the value required for future diffusion barrier applications. The step coverage measured for these systems ranges from generally good (for W-B-N) to exceptional (for W-Si-N). The deposition temperatures of 350°C required for these systems is also generally accepted to be low enough for most envisioned barrier applications. These film and deposition characteristics are very encouraging and work is continuing to determine if these materials may be of use to the semiconductor industry.

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