GROWTH AND PROPERTIES OF W-B-N DIFFUSION BARRIERS DEPOSITED BY CHEMICAL VAPOR DEPOSITION

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ABSTRACT

We have used chemical vapor deposition to grow ternary tungsten-based diffusion barriers to determine if they exhibit properties similar to those of sputter-deposited ternaries. A range of different W-B-N compositions in a band of compositions roughly between 20 and 40% W were produced. The deposition temperature was low, 350°C, and the precursors used are well accepted by the industry. Deposition rates are high for a diffusion barrier application. Resistivities range from 200 to 20000 $\mu\Omega$-cm, the films with the best barrier properties having ~1000$\mu\Omega$-cm resistivities. Adhesion to oxides is sufficient to allow these films to be used as the adhesion layer in a tungsten chemical mechanical polishing plug application. The films are x-ray amorphous as-deposited and have crystallization temperatures of up to 900°C. Barrier performance against Cu has been tested using diode test structures. A composition of $W_{.23}B_{.49}N_{.28}$ was able to prevent diode failure up to a 700°C, 30 minute anneal. These materials, deposited by CVD, display properties similar to those deposited by physical deposition techniques.

INTRODUCTION

There is currently great interest in the chemical vapor deposition (CVD) of diffusion barriers for both aluminum based and future copper based metallization schemes. It has been demonstrated that ternary, refractory based thin films are excellent diffusion barriers to both copper and aluminum [1-6]. In particular the W-B-N system has been studied by Reid et al [7]. However, these materials have typically been deposited by physical deposition and it is not expected that this approach can be used to deposit films with adequate step coverage and barrier properties under the more aggressive aspect ratios and maximum film thicknesses currently envisioned for 0.18 micron geometries and beyond. Films deposited by chemical vapor deposition exhibit superior step coverage's compared with those realized by physical deposition techniques. However, the two deposition techniques are so dissimilar that it is unclear whether or not the excellent barrier characteristics of sputter based ternary refractory alloys will also be displayed films deposited by CVD. Due to the relatively more complex nature of the CVD process, it is also unclear that practically interesting compositions can be obtained using this technique. In the work described below, we have used CVD to grow ternary tungsten-based diffusion barriers to determine if they do, in fact, exhibit properties similar to those of sputter deposited ternaries. We have chosen the W-B-N system since all the components are well known to the semiconductor industry, accepted precursors exist for each component, and there is data indicating that sputtered W-B-N films display excellent barrier properties [7].

EXPERIMENTAL

Six inch wafers were used throughout this work. Depositions were conducted on either thermal oxide, plasma-enhanced CVD oxide or on diode, step coverage, or chemical mechanical polishing test structures. The deposition system was a simple, cold wall, load locked, single wafer reactor. The tungsten precursor was WF_6, which was mixed with a

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combination of SiH$_4$, NH$_3$, and 30% B$_2$H$_6$ in N$_2$. Argon was used as a carrier gas. The Ar, WF$_6$ and SiH$_4$ flows were typically 200, 5, and 3 sccm respectively. The NH$_3$ and B$_2$H$_6$ flows were varied between 10 and 70 sccm. The gases were distributed through separate injection rings spaced 4 inches above the surface of the wafer and were allowed to mix only in the low pressure reaction chamber. The deposition pressure was typically 500 to 700 mTorr. The system was pumped using an oil based mechanical pump. The wafer temperature was typically 350°C. The composition of the films was determined by RBS, ERD and SIMS. Surface morphology and film thickness were determined by SEM. Sheet resistivites were determined with a four point probe. The junctions of the diode test structures were formed by implanting 8x10^{15} As$^+$ cm^2 into a 30 Ω cm, 10 μm p-type epitaxial layer. The junction depth and area are 280 nm and 250 μm x 250 μm. The chemical mechanical polishing test structure consisted of a series of via arrays of various sized holes on a variety of pitches patterned through PECVD oxide down to silicon. Following deposition of the thin film W-B-N diffusion barrier/adhesion layer, 8000Å of CVD tungsten was deposited at 430°C. The wafers were then chemically mechanically polished using a commercially available slurry and tool.

RESULTS AND DISCUSSION

Tungsten was incorporated into the films through the reduction of WF$_6$. Thermodynamics predicts that silane 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 atomic percent. Because B$_2$H$_6$ is unstable at room temperature, we believe that boron was incorporated into the films through simple decomposition of B$_2$H$_6$, possibly catalyzed by the presence of tungsten. Nitrogen was incorporated through the reaction of ammonia with tungsten on the hot wafer surface.

The deposition rates are high for a diffusion barrier application, ranging from 500 to 2000Å per minute. The rate increases with lower flows of ammonia and higher flows of diborane and silane. The films are featureless both visually and under SEM examination, even when one micron thick, Figure 1. The films were blue-gray to brown-gray in color.
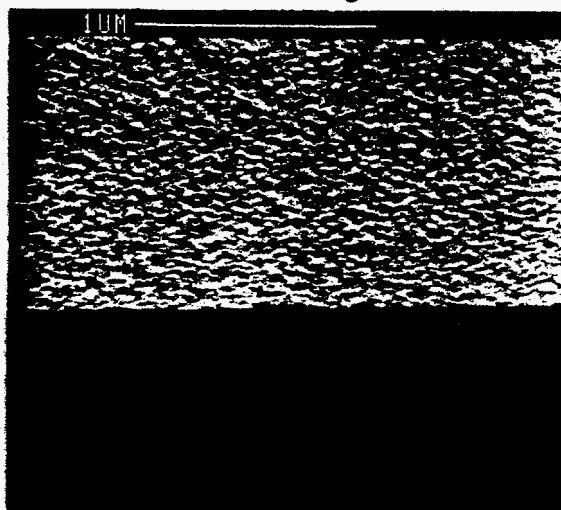

Figure 1.
Surface morphology of a typical film.
Though thick, the film remains smooth
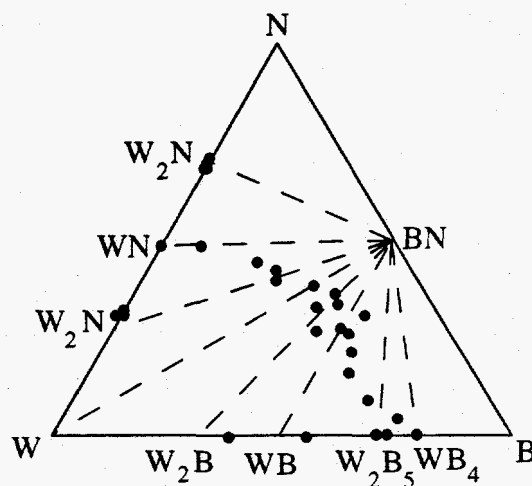without signs of crystallinity or porosity.

Figure 2.
Compositions grown and tentative
system tie lines. We were able to grow
compositions ranging from roughly
WB$_4$ to W$_2$N. (After Reid et al [7])

The compositions grown are indicated on the W-B-N ternary phase diagram, Figure 2. Even though the temperature used was relatively low, there was little hydrogen incorporation in the film, typically ~5% as determined by ERD. We were able to deposit ternary compositions lying in a band roughly between 20 and 40% tungsten. In general, increasing the partial pressure of either B$_2$H$_6$ or NH$_3$ increased the fraction of the appropriate element in the

film. Figure 3 demonstrates this in a plot of fraction N in the film as a function of NH_3 partial pressure. Step coverage was ~30% on samples with aspect ratios of 4.5 and 1 micron diameter. However, the deposition conditions were not optimized for step coverage and we believe that the very high surface area (~450 cm^2) of the test structure used may have degraded the step coverage.

We were unable to increase the tungsten fraction in the film by either increasing the WF_6 partial pressure by a factor of eight or by varying the temperature from ~200°C to ~400°C. At the lowest temperature, the deposited films were unstable in air, possibly due to the presence of unreacted boron or boron hydrides. The exact reason for this restriction in the range of W fraction is unknown, though there is some evidence that it is related to the surface character of the growing film. Figure 4 shows the atomic percent of hydrogen in the growing film as a function of WF_6 partial pressure. Films grown under conditions of higher WF_6 partial pressure had no detectable levels of hydrogen and under these conditions we were unable to grow the ternary, growing instead either W or the binaries. Since H is found in the ternary films deposited under lower WF_6 partial pressure conditions, we speculate that the surface of these growing layers is less densely fluorine terminated. However, as the WF_6 partial pressure is increased, we speculate that the surface becomes fully F terminated. Change in surface termination have been observed in the WF_6-SiH_4 system [8]. We infer from this that growth of the ternary may be affected by the nature of the surface termination.
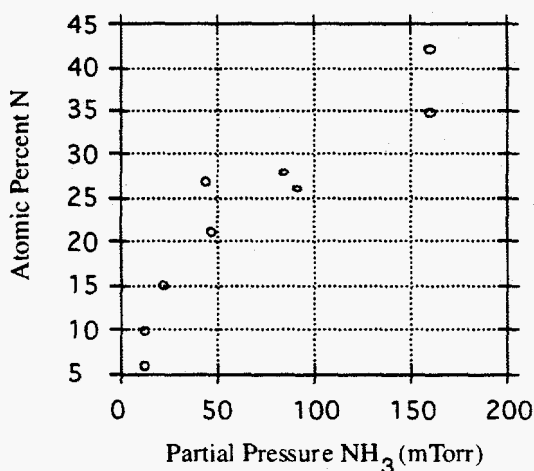

Figure 3.

Plot of fraction N in the film
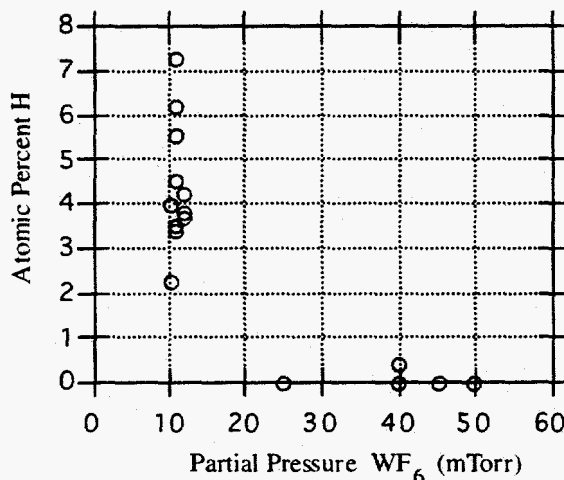as a function of ammonia
partial pressure.

Figure 4.

Plot of %H in the film as a function
of WF_6 partial pressure.

Both SIMS and RBS indicated that the films are uniform through their bulk. The as-deposited films are x-ray amorphous. However, we have been able to identify FTIR transmission peaks associated with B-N bonding using FTIR on samples less than 500Å in thickness.

The as-deposited films have resistivities ranging from 200 $\mu\Omega$-cm for WB_x rich films, to ~20000 $\mu\Omega$-cm for WN_x rich films. Films of intermediate composition with good barrier properties typically had resistivities of ~1000 $\mu\Omega$-cm. In general, ternary films with a higher fraction of "WN_x" displayed a higher resistivity. Resistivity is plotted as a function of fraction N in the film in Figure 5.

Adhesion of the films to thermal and PECVD oxides appears to be acceptable for most compositions, especially when compared to CVD tungsten films. Unlike Ti based materials, the tungsten is unable to reduce the silicon dioxide to improve film adhesion. Bonding in this case may be the result of either B-O or Si-N interactions. As a practical test of adhesion we deposited ~1000Å thick intermediate ternary compositions on a test structure consisting of arrays of holes of varying diameter and pitch. This was immediately followed by the deposition

of 8000Å hydrogen reduced W grown a 3 Torr and 430°C. The tungsten and adhesion layer was then chemically mechanically polished back to the oxide. The end result is shown in figure 6. There was no plug loss, however there was some delamination observed in the ~200µ wide streets between hole arrays. While adhesion appears to be acceptable for certain applications more work is needed in this area to understand and possibly improve adhesion.
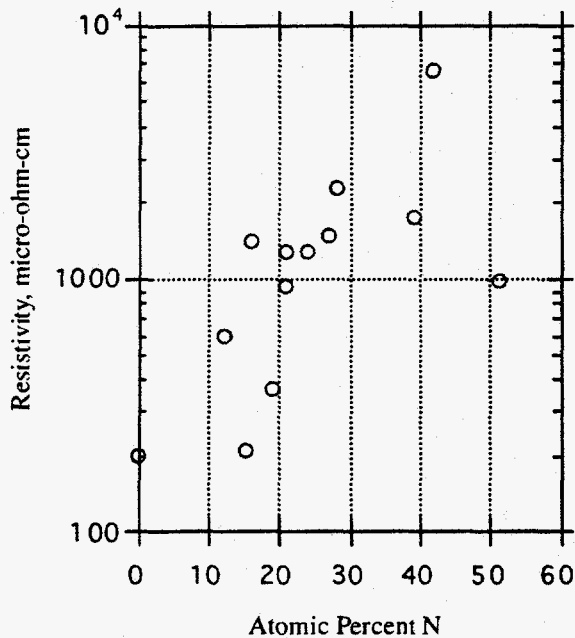

Figure 5.

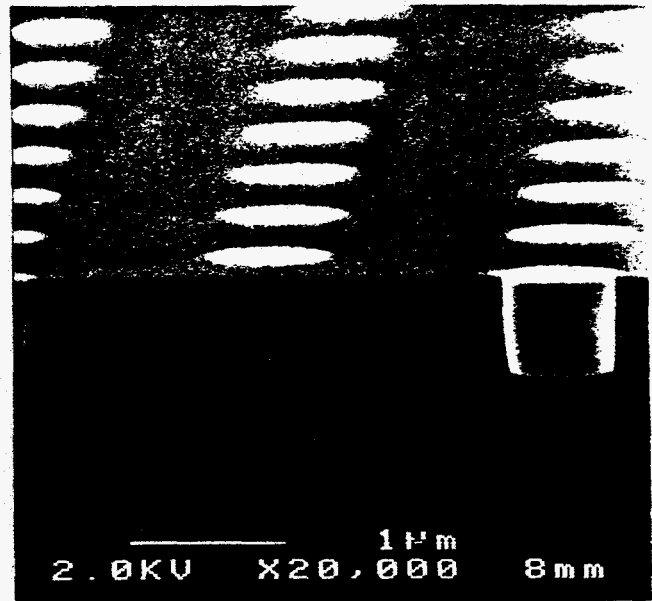Plot of resistivity as a function of N
in the film.

Figure 6.

Tungsten plugs formed by
CMP using $W_{.24}B_{.39}N_{.37}$
as an adhesion-barrier layer.

If it is true that crystalline diffusion barriers fail by the diffusion of species along grain boundaries, then a rough measure of the effectiveness of these as deposited amorphous layers is their crystallization temperature. According to Read camera x-ray diffraction, the as deposited films are x-ray amorphous. Table 1 gives the crystallization temperatures of a range of compositions.

Table 1.

Composition	Diode Temp. (30 min. Vs. Cu)	Crystallization Temp. (1 hour anneal)
$W_{.21}B_{.63}N_{.16}$	<600	<700
$W_{.26}B_{.59}N_{.15}$	<600	
$W_{.24}B_{.66}N_{.10}$	>600	
$W_{.20}B_{.45}N_{.35}$	>600	
$W_{.24}B_{.39}N_{.37}$	>600	>700
$W_{.29}B_{.32}N_{.39}$	>600	>700
$W_{.24}B_{.52}N_{.24}$	>600	<900
$W_{.23}B_{.49}N_{.28}$	~700	

Certain film compositions remain partially amorphous even after a 1 hour anneal at 900°C. This compares very well with ternary diffusion barriers deposited by PVD techniques and is the first indication that these CVD deposited films may have properties similar to ternary PVD materials.

To test these materials resistance to Cu diffusion, diode test structures were used. The thickness of the barrier was 1000Å and the samples were held at temperature for 30 minutes. The results are summarized in Table 1. After anneal, the reverse leakage was measured on eight diodes per composition. The best result obtained was the prevention of diffusion up to 700°C. Films with good barrier properties had compositions slightly more boron rich than the intersection of the W-BN tie line to the band of ternary compositions able to be accessed. The resistivities of these films are roughly $1000\mu\Omega$-cm. While this diffusion barrier performance is not as good as the results obtained with certain of the ternary PVD films, it is very respectable and more than adequate in terms of the thermal budget envisioned for advance Cu and Al metallization processes.

CONCLUSION

A range of different W-B-N compositions in a band of compositions roughly between 20 and 40% W have been produced using CVD. The deposition temperature was low, the precursors used are well accepted by the industry and the deposition rates are high for a diffusion barrier application. Film resistivities range from 200 to 20000 $\mu\Omega$-cm, the films with the best barrier properties having ~1000 $\mu\Omega$-cm resistivities. More work is needed to understand and improve adhesion of these films to oxide, however, compositions displaying good barrier properties have been shown to be adequate for W via CVD and CMP applications. Preliminary results indicate that these materials, deposited by CVD, have barrier properties similar to those deposited by physical deposition techniques. The barrier characteristics observed using diode test structures are more than adequate for future advanced Al or Cu applications.

ACKNOWLEDGMENTS

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