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CHARACTERISTICS OF CVD TERNARY REFRACTORY NITRIDE
DIFFUSION BARRIERS

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ABSTRACT

A range of different ternary refractory nitride compositions have been deposited by CVD (chemical vapor deposition) for the systems TiSiN, WBN, and WSiN. The precursors used are readily available. The structure, electrical, and barrier properties of the films produced by CVD are similar to those observed for films with similar compositions deposited by PVD. The step coverage of the CVD processes developed is good and in some cases, exceptional. A combination of desirable resistivity, step coverage, and barrier properties exists simultaneously over a reasonable range of compositions for each system. Initial attempts to integrate WSiN films into a standard 0.5 μm CMOS process flow in place of a sputtered Ti/TiN stack were successful.

INTRODUCTION

As the critical dimensions for semiconductor devices shrink, new metalization technologies will be required. One future requirement will be advanced diffusion barriers compatible with new metallization schemes. These future barriers will be required to be very thin, $\sim 100\text{\AA}$, in order to keep the interconnect resistivity as low as possible. To ensure barrier uniformity, the barrier morphology will need to be on an even finer scale than the film thickness. A thin film diffusion barrier will further require that the deposition process employed has good step coverage on the aggressive geometries anticipated for advanced ULSI technologies.

Amorphous or nanocrystalline ternary refractory materials have been identified as promising candidates for these barrier applications [1-3]. The attraction of this class of materials is that they do not have the fast diffusion paths present in poly crystalline materials. These materials have been deposited by reactive sputtering. However, it is unlikely that any physical vapor deposition (PVD) process will reliably deposit continuous liners onto high aspect ratio features. Therefore, we have tried to develop chemical vapor deposition (CVD) processes for the systems Ti-Si-N, W-B-N, and W-Si-N which display excellent barrier properties when deposited by PVD. Since PVD and CVD are such different deposition processes, it is unclear whether or not the excellent barrier characteristics of PVD ternary refractory alloys will also be displayed by films deposited by CVD. In addition, the more complex nature of the CVD deposition process makes it unclear whether compositions useful for diffusion barrier applications can be obtained using this technique. In this work we have found that despite the difference in range of compositions accessible by CVD and those reported for PVD, the CVD deposited films display electrical, physical and barrier properties that are strikingly similar to those deposited by PVD. Furthermore, we have

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demonstrated these properties on films deposited by CVD processes with step coverages of up to 100% on aggressive test structures.

EXPERIMENTAL

All of the depositions were performed on 150 mm Si wafers at temperatures between 300 and 450°C, the typical deposition temperature being 350°C. Thermal CVD was used exclusively throughout this work. Depositions were conducted on bare silicon, oxide coated wafers, or on patterned test structures. TiSiN films were deposited in a MRC rotating disk reactor from TDEAT (tetrakis(diethylamido) titanium), NH₃ and SiH₄. The deposition pressure was 20 Torr and the TDEAT bubbler temperature was 80°C. The N₂ carrier gas flow through the bubbler was 0-200 sccm. The pressure in the bubbler was not significantly different than the chamber pressure. Silane flow was typically below 5 sccm and the NH₃ flow was typically 2000 sccm.

The W based films were deposited in a single wafer, cold wall, load locked, reactor. The WBN films were deposited using WF₆, SiH₄, B₂H₆ and NH₃. The NH₃ and B₂H₆ flows ranged from 10 to 70 sccm. The WF₆ and SiH₄ flows were typically 5 sccm and 3 sccm respectively. A 200 sccm Ar flow was used as the carrier gas. The deposition pressure was between 500 and 700 mTorr. The WSiN films were deposited from WF₆, NH₃ and Si₂H₆. The Ar and WF₆ flows were 300 sccm, and 5 to 20 sccm respectively. The NH₃ and Si₂H₆ flows varied between 10 and 150 sccm. The deposition pressure was typically 500 to 700 mTorr. In all these processes, it is important to keep the reactants separate for as long as possible.

The composition of the films was determined by Rutherford backscattering spectrometry (RBS) with 3.5 MeV He and elastic recoil detection (ERD) using 28 MeV Si. Surface morphology and film thickness was determined by SEM. Sheet resistivities were measured using a four point probe. Step coverage was investigated using trench structures cut into the Si substrate which were subsequently oxidized to increase the feature aspect ratio. Film microstructure was determined using transmission electron microscopy (TEM). Plane view samples were analyzed at high resolution, using bright field, electron diffraction and dark field techniques. The samples were also analyzed by x-ray diffraction.

Diode test structures were used to test these materials resistance to Cu diffusion. The junctions of the diode test structures were formed by implanting 8×10^{15} As⁺ cm² 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 thickness of the barrier was 1000Å. The Cu was patterned by liftoff and the anneal time in vacuum was 30 minutes. 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. In the case of WSiN integration studies, CVD WSiN was substituted for a Ti/TiN stack in a M1-via-M2 contact resistivity chain test structure. The plug consisted of chemically mechanically polished CVD W.

RESULTS AND DISCUSSION

Composition

Films of a variety of compositions were deposited for each ternary. In the WBN case we grew compositions lying in a band extending from roughly 75 at.% B on the W-B binary to

2/7

roughly 60 at.% N on the W-N binary. The B rich compositions were easiest to grow. The only impurity found in the film was H which was typically present in concentrations of less than 9 at.%. (The ternary phase diagram of the WBN compositions grown in this study can be found in reference [4]). In the WSiN case we grew compositions ranging in a band from roughly 60 at.% W on the W-N binary to 60 at.% Si on the W-Si binary, Fig. [1]. In this system the process window is widest for N rich films. The only impurity found in the N rich films was less than 5at.% H. For both the WBN and WSiN cases, the band of compositions attainable runs across the proposed system tie lines. For the TiSiN deposit chemistry used, we found that the compositions grown lay in a nitrogen rich band parallel to the tie line between TiN and Si₃N₄, Fig. 2. The amount of N excess depended on the deposition temperature. Growth at 350°C resulted in the lowest N excess. The carbon concentration in these films was less than 1.5 at.%. Hydrogen was found to be present at between 5 and 10 at.%.

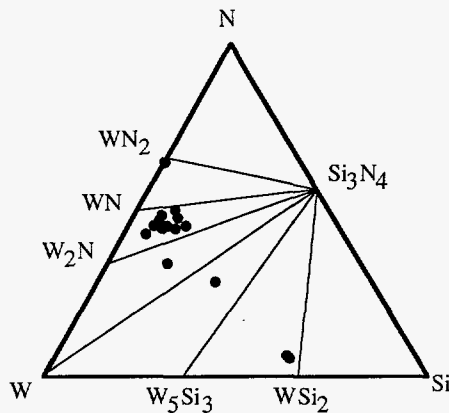


Fig.1

Ternary phase diagram showing
The WSiN compositions grown.

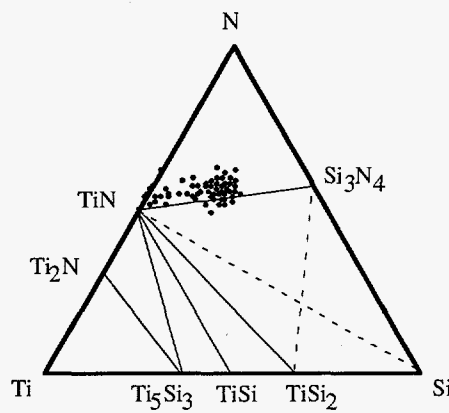


Fig. 2

Ternary phase diagram showing
the TiSiN compositions grown.
The dashed lines are 2 different
proposed tie lines [5].

Structure

Films deposited by CVD with compositions $W_{24}B_{52}N_{24}$, $W_{52}Si_{16}N_{43}$ and $W_{39}Si_{10}N_{41}$ were analyzed by high resolution TEM (transmission electron microscopy). No evidence of any crystallinity was found using electron diffraction, bright field imaging or dark field imaging for either of the WSiN compositions. Figure 2 is a high resolution bright field TEM micrograph of $W_{39}Si_{10}N_{41}$. In the case of $W_{24}B_{52}N_{24}$, small scattered diffracting regions 15-20 Å in size were found. However, the volume fraction of such regions was estimated to be below 0.05, Fig. 3. The TiSiN films displayed a nanocrystalline structure similar to that reported for PVD films, Fig. 4. However, in the case of deposition by CVD less than 4% Si was required to breakup the columnar TiN structure. It is advantageous that any order displayed by the films is significantly less than the film thickness. For the case of advanced diffusion barrier applications this thickness is expected to be on the order of 100Å, which is far greater than the size of any ordered region found in this study. This implies that these films have none of the diffusion short circuits which may be present in barriers with microcrystalline structures. The crystallization behavior of the films is summarized in Table 1. Crystallization temperatures for the WBN layers deposited by CVD are similar to those reported for films deposited by PVD [2].

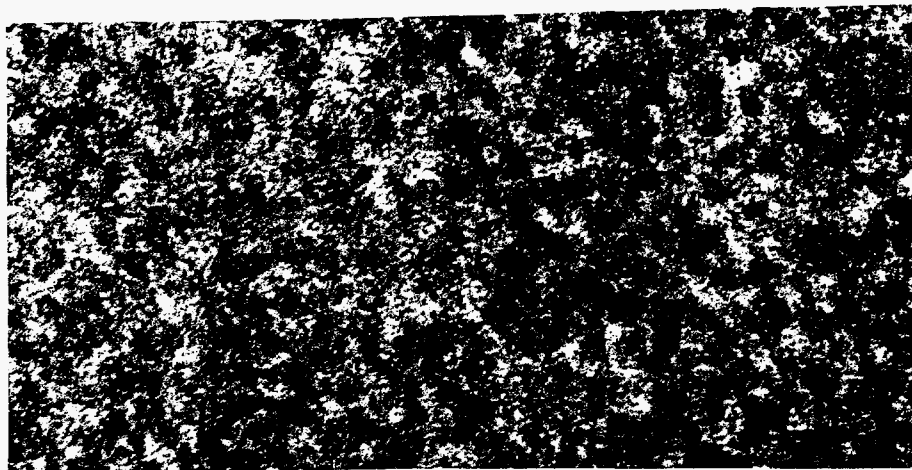


Fig.2 High resolution TEM micrograph showing the structure of a film with composition $W_{39}Si_{10}N_{41}$. No sign of crystallinity was found in either bright field, dark field or electron diffraction modes.

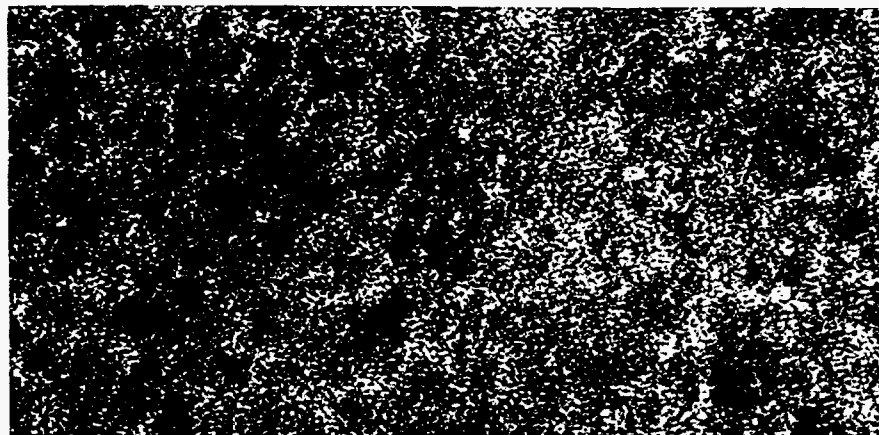


Fig.3 High resolution TEM micrograph showing the structure of $W_{24}B_{52}N_{24}$. Small, scattered diffracting regions 15-20 Å in size were found. However, the volume fraction of such regions was estimated to be below 0.05.

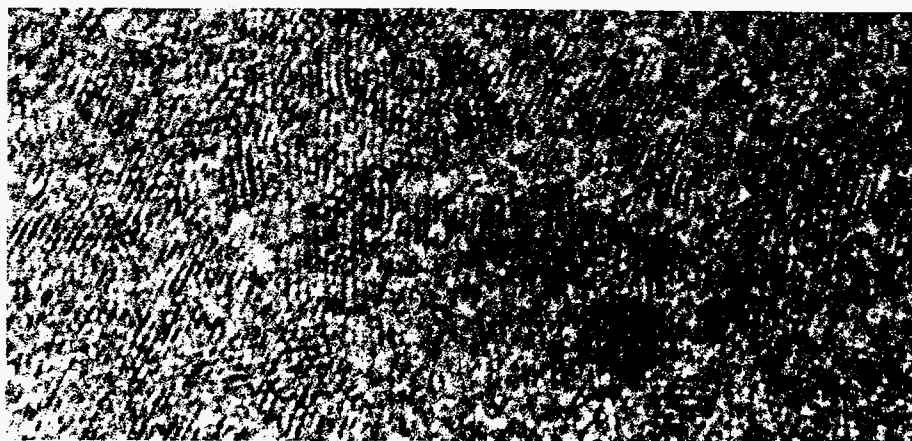


Fig.4 High resolution TEM micrograph showing the nanocrystalline structure of CVD deposited TiSiN containing 4% Si.

The recrystallization temperatures of WSiN films deposited by CVD tend to be lower than those deposited by PVD. The most significant difference found between the PVD and CVD films was that after a 900°C, 1 hour vacuum anneal the major x-ray peaks observed in the CVD WSiN films corresponded to W₂N or beta W. For the PVD WSiN films only alpha W was reported after a similar anneal [1].

Resistivity

Since the range of compositions grown by CVD were typically different from those reported in the literature for PVD, it is difficult to make one to one property comparisons between films deposited by the different techniques. However, both the range of resistivities and the resistivities of films with similar compositions deposited by either CVD or PVD showed similar results for each ternary system.

In the case of WBN, the resistivities of ternary films typically ranged from 200 to 2000 μΩ cm. Films with higher N content had higher resistivities [4]. While there is more scatter in the CVD results, the trend and range of resistivities is similar to that observed in PVD films [2]. In the case of the WSiN system, the resistivity of ternary films deposited by CVD ranged from 350 to 1200 μΩ cm. Increasing the silicon content in the films was found to increase their resistivity. Again films deposited by CVD showed similar properties as those deposited by PVD[1]. In the TiSiN system, the resistivity was a strong function of N and Si content. The resistivity sharply increased for a constant Si to Ti ratio as the N content increased. For a fixed excess of N above the SiN-TiN tie line, increasing the fraction of Si in the film increased the resistivity. A similar trend has been observed in films deposited by PVD [3].

Table 1

The film thickness was 1000Å. The diodes were annealed in vacuum. The films were also heated in vacuum to determine the crystallization temperature.

Composition	Diode Failure Temp. (30 min. Vs. Cu)	Crystallization Temp. (1 hour anneal)
W ₂₁ B ₆₃ N ₁₆	<600	<700
W ₂₄ B ₆₆ N ₁₀	>600	
W ₂₄ B ₃₉ N ₃₇	>600	>700
W ₂₄ B ₅₂ N ₂₄	>600	<900
W ₂₃ B ₄₉ N ₂₈	~700	
W ₄₇ Si ₉ N ₄₄	700	~700

Barrier Properties

The results of the barrier studies using large area diode leakage test structures are given in Table 1. The thickness of the barrier was $\sim 1000\text{\AA}$. Again, the performance of CVD films are comparable to that of PVD films of similar composition. For most compositions, the diode failure temperature is significantly higher than that envisioned for any copper metallization process.

Integration with W CVD and Al Metallization

Both $W_{45}Si_{10}N_{45}$ and $W_{24}B_{39}N_{37}$ have been integrated with W CVD and chemical mechanical polishing. In the case of $W_{45}Si_{10}N_{45}$, M1-via-M2 chains were fabricated using a standard CMOS $0.5\ \mu\text{m}$ technology with AlCu metallization. Via resistivities ranged from equivalent to roughly an order of magnitude higher than those obtained using sputtered Ti/TiN. This result is similar to that obtained using selective W plugs to Al [6]. The reason for the increased scatter is under investigation and is probably the result of poor cleaning of the bottom of the contact before deposition of the WSiN. Adhesion of both types of films was sufficient to prevent delamination during both W CVD and W chemical mechanical polishing. This result indicates that neither the formation of AlF_x from the reaction of Al and WF_6 , or the reaction of Al in the presence of NH_3 to form AlN, are expected to be serious problems. Interestingly, it was found to be somewhat more difficult to nucleate the CVD W on the WSiN layer than it was to nucleate deposition on the standard sputtered TiN layer.

Step Coverage

The physical, electrical and barrier properties of films deposited by PVD and CVD appear to be surprisingly similar. The major advantage of the CVD process is that it offers improved step coverage compared with PVD. In the case of the TiSiN system, addition of SiH_4 to TDEAT and NH_3 significantly increases step coverage over that observed in the absence of SiH_4 . Step coverage was 75% on trenches with an aspect ratio of 6 and a trench opening of $0.2\ \mu\text{m}$. Step coverage of the WBN process was determined to be 40% on vias with an aspect ratio of 5.5. The step coverage of WSiN films with concentrations of Si $< 10\%$ was found to be 100%, Fig. 4. This extreme step coverage is hypothesized to be the result of NH_x fragments adsorbing on the surface and reducing the sticking coefficient of the other species.

CONCLUSIONS

Ternary refractory nitrides have been successfully deposited by CVD for the systems TiSiN, WBN, and WSiN. The structure, electrical, and barrier properties of the films produced by CVD are similar to those observed for films with similar compositions deposited by PVD. The advantage offered by CVD is enhanced, and in some cases, exceptional step coverage. A combination of desirable resistivity, step coverage and barrier properties exists simultaneously over a reasonable range of compositions for each systems investigated. Initial attempts to integrate WSiN films into a relatively standard $0.5\ \mu\text{m}$ CMOS process flow in place of a sputtered Ti/TiN stack are encouraging.

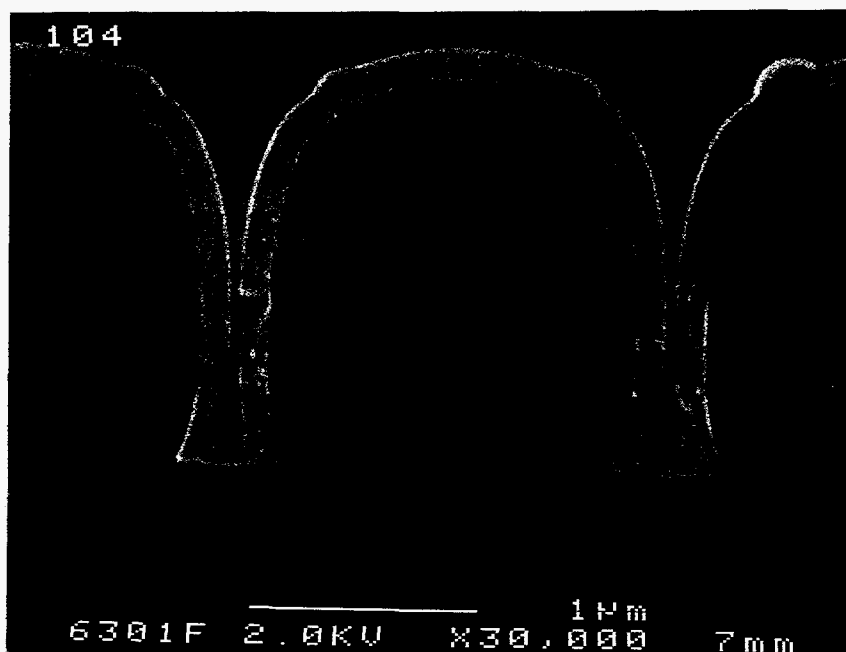


Fig.4.

Step coverage of a film deposited from WF₆, Si₂H₆ and NH₃ with composition W₄₆N₄₆Si₈. The deposition temperature was 350°C.

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