Tantalum Nitride Films Grown by Inorganic Low Temperature Thermal Chemical Vapor Deposition

Diffusion Barrier Properties in Copper Metallization

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Key findings are presented from a systematic study which evaluated the performance of chemical vapor deposited (CVD) nitrogen-rich tantalum nitride (TaN_x , $x \sim 1.8$) films as a diffusion barrier in copper (Cu) based metallization schemes. For this purpose, 3800 Å thick Cu films were grown by physical vapor deposition (PVD) on 550 Å thick TaN_x films which were deposited by low temperature (<425°C) thermal CVD (TCVD) using tantalum pentabromide (TaBr_5), ammonia, and hydrogen as coreactants. The resulting stacks were annealed in argon ambient at 450, 500, 550, and 650°C for 30 min each, along with similar PVD Cu/PVD TaN_x bilayers of identical thickness. Both types of pre- and postannealed stacks were characterized by X-ray photoelectron spectroscopy, Auger electron spectroscopy, Rutherford backscattering spectrometry, nuclear reaction analysis for hydrogen profiling, X-ray diffraction, stack sheet resistance measurements, and Secco chemical treatment and etch-pit observation by scanning electron microscopy. The resulting findings showed that the PVD TaN_x films provided an excellent barrier against Cu diffusion throughout the annealing window investigated. Alternatively, the TCVD TaN_x films exhibited similar stability up to 550°C. Barrier failure occurred, however, at temperatures between 550 and 600°C, as revealed by the formation of etch pits after Secco etch treatment. The failure of the TCVD TaN_x films could not be attributed to bromine incorporation, given that residual bromine (~0.5 atom %) in the TCVD TaN_x films was highly stable against thermal diffusion in the temperature window investigated. Instead, the higher thermal stability of the PVD TaN_x was attributed to differences in film microstructure and crystalline phase, or the location of excess nitrogen within the film matrix.
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As the microelectronics industry evolves into ultralarge scale integration (ULSI) device schemes, copper (Cu) appears to provide better performance as an interconnect material than the currently used aluminum (Al) alloys. In this respect, Cu offers lower resistivity and enhanced electromigration resistance than its Al counterpart.¹ Unfortunately, Cu is known to be highly reactive with and a fast diffuser in silicon. Its presence in silicon leads to the formation of deep trap levels, which severely degrade device performance.² Clearly, a critical issue in the realization of structurally stable copper-based metallization architectures is the development of an appropriate diffusion barrier which prevents undesirable interactions between Cu and the semiconductor and dielectric regions of the computer chip.

In order to address this issue, various refractory metals and their binary nitrides, as well as ternary metal-silicon-nitrogen compounds, have been heavily examined. Of these materials, tantalum (Ta)-based compounds are considered perhaps among the most promising candidates. Tantalum and its nitrides are highly refractory materials that are stable to extremely high temperatures.³ Additionally, they are known to be thermodynamically stable with respect to Cu, as documented by the absence of Cu-Ta or Cu-N compounds. This stability is supported by a large number of studies pertaining to the appropriateness of Ta compounds as copper diffusion barrier. For instance, a sputtered 50 nm thick Ta barrier has demonstrated its resistance to Cu diffusion up to 550°C for 1 h.⁴ In this respect, tantalum nitrides could provide even higher resistance to diffusion as compared to the pure metal, because of their dense interstitial crystalline structure.⁵ As a result, sputtered tantalum nitrides have been successfully shown to act as good diffusion barriers in Cu technology, with proven Cu-TaN contact stability to temperatures as high as 750°C.²

Conventional forms of physical vapor deposition (PVD) of TaN_x , including collimated sputtering, are inherently incapable of conformal step coverage in aggressive trench and via structures, given their "line of sight" type approach. Alternative processing techniques are thus

required for producing Ta-based liners for incorporation in subquarter-micron device technologies. In this respect, chemical vapor deposition (CVD) is one of the most promising techniques. CVD exhibits an intrinsic potential for conformal coverage, in view of the "catalytic" role that the substrate plays in the deposition reaction.

Numerous CVD approaches have already been investigated for the growth of tantalum nitride. Inorganic CVD from tantalum pentachloride (TaCl_5) led to the deposition of tantalum nitride at temperatures above 600°C.⁶ Clearly, this high processing temperature prohibits the use of this deposition methodology in actual semiconductor devices. Metallorganic CVD (MOCVD) approaches, on the other hand, included the use of various precursors such as the dialkylamido Ta complex,⁷ $\text{Ta}(\text{NEt})(\text{NEt}_2)_3/\text{Ta}(\eta^2\text{EtN}=\text{CMeH})(\text{NEt}_2)_3$ blend,⁸ and $\text{Ta}=\text{NBu}^t(\text{NEt}_2)_3$,⁹ etc. Unfortunately, various issues, including high deposition temperature (>500°C), the incorporation of up to 40 atom % hydrogen, and the inclusion of several atomic percent of C and O seriously limited their technological usefulness.

In view of these issues, work by the present investigators has focused on the development of a low temperature thermal CVD (TCVD) process which employs simple inorganic Ta compounds. The latter are selected with primary bonds that are relatively weak. Such bonds are thus easily cleaved at low temperature, and their recombination can be interrupted by the presence of nitrogen to yield tantalum nitride. A candidate compound of this type is tantalum pentabromide (TaBr_5). The heat of formation for TaBr_5 is -143 kcal/mol, as compared to -205 kcal/mol for TaCl_5 ,¹⁰ implying that TaBr_5 could potentially decompose at appreciably lower temperature than TaCl_5 .

This paper is the second in a series of reports on the identification and optimization of a low temperature inorganic TCVD route to TaN_x using TaBr_5 , ammonia (NH_3), and (H_2) as coreactants.¹¹ The first report focused on the development of a low temperature TCVD process for the deposition of amorphous TaN_x films with C, O, and Br contamination levels below 1 atom %, and better than 95% step coverage in nominally 0.3 μm , 4.5:1 aspect ratio structures.¹¹ In this article, key experimental details and associated findings are presented from a study which employed conventional PVD-grown TaN_x as

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Table I. Summary of process parameters for TCVD TaN_x, PVD TaN_x, and PVD Cu films.

TCVD TaN _x		PVD TaN _x		PVD Cu	
Parameter	Value	Parameter	Value	Parameter	Value
Carrier gas	H ₂ (60 sccm)	Sputtering gas	Ar (50 sccm)	Sputtering gas	Ar (40 sccm)
Reactant gas	NH ₃ (350 sccm)	Reactant gas	N ₂ (55 sccm)	Reactant gas	none
Deposition pressure	0.4 Torr	Deposition pressure	5 mTorr	Deposition pressure	4 mTorr
Base pressure	10 ⁻⁶ Torr	Base pressure	10 ⁻⁸ Torr	Base pressure	~10 ⁻⁸ Torr
Substrate temperature	425°C	Substrate temperature	25°C	Substrate Temperature	25°C
Source temperature	160°C	Plasma power (dc)	2 kW	Plasma power (dc)	2 kW

baseline, and which aimed to establish a thorough assessment of the performance of the TCVD-grown TaN_x from TaBr₅ as diffusion barrier in Cu metallization.

Experimental

Description of processing conditions.—In a first step, 550 Å thick TCVD and PVD TaN_x films were deposited on Si(100) substrates. Prior to deposition, the Si substrates received a standard organic clean process consisting of a 1 min bath in trichloroethylene, acetone, and then methanol, followed by 10% HF clean to remove native oxide. All samples were subsequently in situ plasma cleaned in their respective CVD and PVD processing modules prior to actual deposition. In the case of TCVD TaN_x films, processing was performed in a custom-designed, warm wall, plasma capable, stainless steel CVD reactor. Relevant details of the deposition process have been described elsewhere and are not reported herein.¹²

In the case of PVD TaN_x, conventional sputter deposition was carried out in a commercial Varian MB² cluster tool system using an electronic grade Ta target. The target was in a nitrided mode during actual deposition. Table I summarizes the key process parameters for the deposition of TCVD and PVD TaN_x films.

In a second step, the PVD and TCVD TaN_x films were exposed to 30 min anneals each in an argon ambient at temperatures of 450, 500, 550, 600, and 650°C. The goal was to explore and document any thermally induced compositional or structural changes in the TaN_x films that might influence the subsequent Cu/TaN_x stack annealing studies.

In a third step, the as-deposited PVD and TCVD TaN_x films were processed to deposit 3800 Å thick Cu films by noncollimated sputtering to form Cu/TaN_x/Si contact systems. Cu deposition was carried out in a commercial CVC connection cluster tool, using the process parameters listed in Table I. The resulting Cu/TaN_x stacks were subsequently annealed in Ar ambient for 30 min each at five settings: 450, 500, 550, 600, and 650°C.

Description of characterization techniques.—A thorough evaluation of the microchemical, microstructural, and barrier properties of all TaN_x films was carried out at the analytical facilities of the New York State Center for Advanced Thin Film Technology. The analytical techniques used included Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Ruther-

ford backscattering spectrometry (RBS), X-ray diffraction (XRD), four-point resistivity probe, nuclear reaction analysis (NRA) for hydrogen profiling, and scanning electron microscopy (SEM). Key details of the analytical methods applied have already been discussed elsewhere.¹²

Additionally, etch pit observation was performed by selectively removing the Cu and TaN_x layers, in a first stage, using a wet chemical etch solution consisting of a 1:1 ratio of nitric acid (HNO₃) and distilled water [H₂O for Cu and 49% hydrofluoric acid (HF) in distilled H₂O for TaN_x]. The Si substrates were then exposed for 5 s to a Secco etch solution which consisted of one part by volume of 0.15 M potassium dichromate (K₂Cr₂O₇) in H₂O and two parts HF.¹³

Results and Discussion

Characterization of pre- and postannealed TaN_x films prior to Cu processing.—Table II summarizes the properties of as-deposited TCVD and PVD TaN_x films. Prior to Cu deposition and annealing experiments, both types of TaN_x films were exposed to the same annealing recipes used for the Cu/TaN_x/Si contact systems, namely, 450 to 650°C in 50°C steps. The purpose was to establish baseline performance metrics, and determine the effects of thermal treatment on key TaN_x films characteristics, including Br concentration and film microstructure.

For illustration purposes, Fig. 1 displays the RBS spectra of TCVD TaN_x as-deposited and after annealing at 650°C. There was no change observed in Br concentration and peak profile before and after all annealing steps. This finding supports the expectation that small bromine concentration might require appreciably high thermal energy to diffuse out of the TaN_x lattice, and are thus expected to have no negative effect on Cu/TaN_x/Si material reliability.

Figure 2 exhibits the XRD spectra of PVD TaN_x before annealing (a) and after annealing at 450°C (b) and at 650°C (c). The XRD spectrum of the as-deposited film consisted primarily of broad reflection peaks that correspond to a nanocrystalline cubic TaN phase, possibly within an amorphous matrix. The XRD reflection peaks became increasingly sharper and more intense with higher annealing temperature. In particular, the full-width-at-half-maximum (fwhm) for the TaN (111) peak decreased continuously from 2.42° for the as-deposited film to 1.81° for the film annealed at 650°C. This was accompanied

Table II. Relevant properties for TCVD and PVD TaN_x films.

Property (analytical technique)	TCVD TaN _x	PVD TaN _x
Thickness (RBS)	550 Å	550 Å
Stoichiometry (AES)	TaN _{1.83±0.12}	TaN _{1.71±0.09}
Density (g/cm ³) (SEM + RBS + AES)	9.70	10.17
Light element impurities (AES and XPS)	C below detection limits O < 2.5 atom %	O and C below detection limits
Hydrogen incorporation (hydrogen profiling)	<1 atom %	~1 atom %
Heavy element incorporation (XPS, RBS)	≤0.5 atom % Br, Ar below detection limits	~1 atom % Ar, Br below detection limits
Structure (XRD)	amorphous	Nanocrystalline cubic TaN phase within an amorphous matrix
Resistivity (four-point probe)	~2500 μΩ cm	~3100 μΩ cm
Phase (XPS)	Mixture of phases	Mixture of phases

Figure 1. Typical RBS spectra for PVD Ta_xN_y films: (a) as-deposited and (b) annealed at 650°C. The Br RBS peak is shown magnified in the insets.

by the detection of very weak and broad peaks that correspond to a Ta_3N_5 phase.

Similarly, Fig. 3 displays the XRD spectra for TCVD Ta_xN_y before (a) and after annealing at 450 (b), 650 (c), and 700°C (d). There were no observed changes between the XRD profiles of the as-deposited samples and the samples annealed up to 600°C, with all samples exhibiting the characteristic XRD spectrum of a mainly amorphous phase. Crystallization of the films was detected between 600 and 650°C annealing temperature. Further annealing at 700°C for 30 min in Ar ambient led to the identification of a dominant Ta_3N_5 structure in coexistence with hexagonal TaN.

Diffusion barrier performance of PVD Ta_xN_y .—Figure 4 presents the RBS spectrum of postannealed (650°C) Cu/PVD Ta_xN_y /Si stacks after Cu strip, with the Ar and Cu peaks shown magnified in the inset. No changes were observed in the RBS spectra of the as-deposited PVD Ta_xN_y films and those exposed to Cu deposition and annealing up to 650°C. This finding is supported by the RBS studies of Holloway et al.⁵ which showed Ta outdiffusion to the Cu surface for the Cu/Ta/Si material system after thermal treatment at 550°C. This motion was followed by the migration of Cu through the Ta barrier to the Si interface and the formation of a Cu_3Si phase. This phenome-

Figure 2. X-ray diffraction patterns of PVD Ta_xN_y films: (a) as-deposited, (b) annealed at 450°C, and (c) annealed at 650°C.

Figure 3. X-ray diffraction patterns of TCVD Ta_xN_y films: (a) as-deposited, (b) annealed at 450°C, (c) annealed at 650°C, and (d) annealed at 700°C.

Figure 4. RBS spectra of a Cu/PVD Ta_xN_y /Si stack after annealing at 650°C, and subsequent Cu strip. The Ar and Cu peaks are shown magnified in the inset.

Figure 5. XPS depth profile of a Cu/PVD TaN_x/Si stack after annealing at 650°C and subsequent Cu strip.

non was suppressed in the case of the Cu/Ta₂N/Si system, where Ta₂N exhibited thermal stability up to 650°C.

Our RBS results were supported by the XPS results shown in Fig. 5, which displays XPS depth profile for postannealed (650°C) Cu/PVD TaN_x/Si after Cu strip. No Cu or Ta diffusion was observed within the detection limits of XPS. Similarly, XRD investigations of Cu/PVD TaN_x/Si stacks confirmed the RBS and XPS data, as shown in the XRD spectra of Fig. 6a and b for Cu/PVD TaN_x/Si stacks before (a) and after annealing at 650°C (b). Strong Cu(111), Cu(200), and Cu(220) reflection lines are seen, along with weak and broad TaN_x peaks. XRD did not detect the presence of any phase formation and confirmed the high thermal stability of Cu/PVD TaN_x/Si stacks. No etch pits were observed by SEM after Secco etch treatment of the Cu/PVD TaN_x/Si system, even for the samples annealed at 650°C.

Diffusion barrier performance of TCVD TaN_x.—The work discussed above was repeated for Cu/TCVD TaN_x/Si stacks. In this respect, XPS did not indicate any Cu or Ta interdiffusion even after the 650°C thermal treatment step, as shown in Fig. 7 which displays the XPS depth profile for postannealed (650°C) Cu/TCVD TaN_x/Si after Cu strip. No Cu was detected in the TaN_x or Si within the detection limits of XPS (~1 atom %). XRD yielded the same results as in the case of PVD TaN_x. As illustration, Fig. 8 presents the XRD spectra of as-deposited (a) and after 650°C annealed (b) Cu/TCVD TaN_x/Si stacks after Cu strip. No material interaction or phase formation were seen in the XRD spectra, even after the 650°C anneal. The strong reflection peaks in Fig. 8 corresponded to Cu (111), Cu (200), and Cu (220), while the broad and weak peaks were due to TCVD TaN_x.

Figure 6. XRD spectra of a Cu/PVD TaN_x/Si stack: (a) as-deposited and (b) annealed at 650°C.

Figure 7. XPS depth profile of a Cu/TCVD TaN_x/Si stack after annealing at 650°C and subsequent Cu strip.

RBS analysis yielded, on the other hand, different results as documented in Fig. 9a–d. These figures display the magnified Ar, Cu, and Br RBS peaks in TCVD TaN_x after Cu strip for, respectively, as-deposited and annealed (550, 600, and 650°C) Cu/TCVD TaN_x/Si stacks. No change was observed in the spectra up to 550°C thermal treatment. However, at higher annealing temperatures, the Cu peak increased in width and intensity, indicating the motion of small amounts of Cu into the TaN_x films. In this respect, Fig. 10 plots the RBS integrated Cu peak intensities in both PVD and TCVD films as a function of annealing temperature. A marked increase in the number of Cu counts is observed for the TCVD TaN_x film after the 650°C annealing step.

Secco etching of the Cu/TCVD TaN_x/Si contact systems did not reveal any etch pits in Si for samples heat-treated up to 550°C, as shown in the SEM micrograph of Fig. 11. Alternatively, SEM micrographs of similar samples revealed the presence of rectangularly shaped etch pits in Si, with the size of a few microns after treatment at higher temperature. This is illustrated in Fig. 12 and 13 for the samples treated at, respectively, 600 and 650°C.

Discussion

The results reported above indicate that the PVD and TCVD TaN_x films exhibited different diffusion barrier performance in Cu metalization, with the TCVD TaN_x film beginning to fail above 550°C, while its PVD counterpart shows thermal integrity up to 650°C. This

Figure 8. XRD spectra of a Cu/TCVD TaN_x/Si stack: (a) as-deposited and (b) annealed at 650°C.

difference in behavior could not be attributed to the presence of bromine in the TCVD TaN_x , given that no variations in Br concentration or peak profile were observed even after thermal treatment at 650°C . The high thermal stability of Br was seen for annealed TCVD TaN_x both before Cu deposition, as documented in the RBS spectra of Fig. 1, and after Cu deposition, followed by Cu/TCVD TaN_x /Si stack anneal, and Cu strip. The same expectation applies to other impurities in the TaN_x films, given that their concentrations were too small to significantly influence barrier properties.

In terms of thermal stress behavior, two competing breakdown mechanisms were reported for different phases of tantalum nitride. In the case of stoichiometric TaN, Cu was found to migrate into the Si substrate without reacting with the barrier layer. In comparison, Ta_2N failed due to an interfacial reaction between Si and the barrier layer, followed by Cu diffusion to the interface. The failure mechanism in this case was independent of whether the barrier was amorphous¹⁴ or

crystalline.² In our case, no reaction was observed between Si and either the PVD or TCVD TaN_x barrier, and no tantalum silicide was detected regardless of the thermal treatment applied. Furthermore, density variations between the two types of films were not significant enough to justify the marked difference in barrier performance.

The different thermal stress behaviors of the TCVD and PVD TaN_x films could be attributed to the observed differences in their microstructure, and resulting variations in crystallization behavior as seen in Fig. 2 and 3. In this respect, no abrupt change was seen in the microstructure of the PVD films with annealing temperature. Primarily, a nanocrystalline cubic TaN phase was detected in the as-deposited films, with a slow evolution in grain size growth occurring with higher temperatures. Conversely, the TCVD films exhibited an amorphous structure up to 600°C , with crystallization into a predominantly Ta_3N_5 phase in co-existence with a hexagonal TaN matrix occurring above that temperature. It is suggested that crystallization of the

Figure 9. (a, top left) Magnified Ar, Cu, and Br RBS peaks for an unannealed TCVD TaN_x film after Cu deposition and subsequent Cu strip. (b, top right) Magnified Ar, Cu, and Br RBS peaks for a TCVD TaN_x film, after Cu deposition, annealing at 550°C , and subsequent Cu strip. (c, bottom left) Magnified Ar, Cu, and Br RBS peaks for a TCVD TaN_x film, after Cu deposition, annealing at 600°C , and subsequent Cu strip. (d, bottom right). Magnified Ar, Cu, and Br RBS peaks for a TCVD TaN_x film, after Cu deposition, annealing at 650°C , and subsequent Cu strip.

Figure 10. Integrated RBS Cu peak intensities in PVD and TCVD TaN_x as a function of annealing temperature. Data is shown for films after Cu deposition, Cu/TaN_x stack anneal, and subsequent Cu strip.

amorphous TCVD films, and the associated formation of grain boundaries, might have provided a path for Cu diffusion.

Alternatively, even though both types of TaN_x films were highly N rich, the location of excess N within the film matrix might have been different. In the case of the TCVD films, the N:Ta ratio was close to Ta₃N₅, and the films ultimately crystallized into a predominant Ta₃N₅ phase. In contrast, the PVD films were mainly cubic TaN, which clearly corresponds to a 1:1 ratio for N:Ta. This implies that the excess N in the PVD TaN_x might have been located interstitially, and at the grain boundaries of the TaN_x matrix. As such, it might have “stuffed” the grain boundaries and acted as a good barrier against diffusion along such pathways.

Nevertheless, both contact systems, namely, Cu/PVD TaN_x/Si and Cu/TCVD TaN_x/Si were stable up to 550°C, a temperature well in excess of those experienced during the integrated circuitry fabrication flow.

Conclusions

A systematic evaluation was carried out of the barrier characteristics of nitrogen-rich TaN_x films grown by conventional PVD and

Figure 11. SEM micrographs of the Si surface after Secco etch for a Cu/TCVD TaN_x/Si stack annealed at 550°C.

Figure 12. SEM micrographs of the Si surface after Secco etch for a Cu/TCVD TaN_x/Si stack annealed at 600°C.

low temperature inorganic CVD from TaBr₅. The study demonstrated that the TCVD and PVD TaN_x films were stable against Cu diffusion up to temperatures of, respectively, 550 and 650°C. The lower thermal performance of the TCVD films could not be attributed to the presence of bromine, given the high stability of Br against migration to temperatures in excess of 650°C. Instead, it is suggested that variations in film microstructure or the location of excess N in the TaN_x matrix might have played a primary role in the observed difference in barrier performance.

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Figure 13. SEM micrographs of the Si surface after Secco etch for a Cu/TCVD TaN_x/Si stack annealed at 650°C.

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