Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 309–311

Comparison of CVD and PVD TaN as Diffusion Barriers for Al and Cu Metallization

S. C. Sun, M. H. Tsai, C. E. Tsai*, and H. T. Chiu*

National Nano Device Laboratory and Department of Electronics Engineering
** Institute of Applied Chemistry*
National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

A comparison of MOCVD Tantalum nitride (TaN) and PVD TaN as diffusion barriers for Al and Cu metallization was evaluated by electrical measurements on shallow p^+n diodes structures. SEM, XRD and SIMS analysis were performed in conjunction with electrical measurements in the degradation study of Al/TaN/Si and Cu/TaN/Si contact structures. Results indicate that PVD TaN possesses a higher thermal stability than CVD TaN against Al and Cu diffusion. This is attributed to the microstructural differences in the two types of films.

I. INTRODUCTION

Transition metal nitrides are attractive candidates as diffusion barriers owing to their high conductivity, high thermal stability and resistance to diffusion of foreign atoms [1,2]. Among them, tantalum nitride has received great interest because it would not form compound with copper [3]. TaN deposition can be accomplished through either chemical vapor deposition (CVD) or physical vapor deposition (PVD) method. Previous studies of reactive sputtered TaN and Ta_2N have reported that they were excellent metallurgical diffusion barriers between copper and Si [4,5] and between aluminum and Si substrates [6,7]. The main drawback of PVD process is its lack of conformality. The poor step coverage of reactive sputtering process may be reaching its limit of usefulness in the small feature size (< 0.35 μm) and high aspect ratio contact and via holes. Accordingly, chemical vapor deposition has attracted large interests due to its superior conformality. Recently we have developed a low-resistivity CVD cubic-phase TaN process using a new metalorganic precursor tertbutylimido-tris-diethylamido-tantalum (TBTDET) [8]. This process differs from an earlier attempt to grow TaN by CVD method using $Ta(NMe_2)_5$ and ammonia chemistry, which has resulted in a high-resistivity tetragonal phase Ta_3N_5 films [9].

In this paper, we report the effectiveness of both CVD and PVD TaN films as diffusion barriers in the contact structures of Al/TaN/Si and Cu/TaN/Si from p^+n junction diode leakage measurements. Furthermore, SEM, XRD and SIMS are employed to study the failure mechanisms.

II. EXPERIMENTAL

Phosphorus-doped (100) Si substrates of 10~20 Ω-cm were prepared. A CVD or PVD TaN barrier layer of 60 nm thickness was then deposited. The deposition of CVD TaN was carried out in a cold-wall, low-pressure CVD reactor. The base pressure was maintained at 1×10^{-5} torr by a diffusion pump. Liquid precursor TBTDET was contained in a glass vessel and heated to 40 °C. Prior to deposition, an in-situ H_2 bake and argon sputtering were carried out in the LPCVD reactor by controlling the rf power density to remove the native oxide on the silicon surface. CVD film was grown at a temperature of 650 °C and a pressure of 20 mtorr.

PVD films wrere deposited by reactive sputtering of Ta target in a gas mixture of argon to nitrogen ratio equal to 3/1 ambient at a pressure of 8 mtorr. The base pressure was maintained at 1×10^{-6} torr. The samples were exposed to the air before 400 nm copper or aluminum was deposited. Film thickness was measured by SEM. The resistivity was measured by four-point probe. Impurity profiles were obtained from Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and wavelength dispersive spectroscopy (WDS). Interdiffusions of Cu and Si in the TaN as well as Al and Si in the TaN films were further analyzed by SIMS measurements using Cameca IMS4F with an O_2^+ ion beam at 36° incident angle. The surface morphology was observed by SEM and atomic force microscopy (AFM).

p^+n junction diodes used in the electrical evaluation were first implant with BF_2^+ of 50 KeV and a dose of 3×10^{15} cm^{-2}. The samples were annealed at 900 °C for 30 min in nitrogen. TaN barrier layers were subsequently deposited in the contact structures using either CVD or PVD technique. 400 nm-Cu or Al was sputtered on top of 60-nm TaN films. TaN was etched by SF_6 plasma after Cu or Al patterns were defined. Samples were then thermally annealed at temperatures ranging from 400 to 650 °C in vacuum for Cu and in N_2

for Al metallization. The leakage current was measured using HP4145B at 5V reverse bias for thermal stability study.

III. RESULTS AND DISCUSSION

Fig. 1 (a) shows the planeview of TEM micrograph of a 60-nm CVD TaN film. The grain sizes distributed uniformly between 50 to 70 nm. Fig. 1 (b) shows the planeview TEM micrograph of a 60-nm PVD TaN film with a more compact grain structure and an average grain size of 20 nm. The electronic diffraction patterns (not shown) for both CVD and PVD TaN are f.c.c. NaCl structures. The apparent difference between these two films is that CVD TaN contains larger and more loosely-packed grains than PVD TaN films.

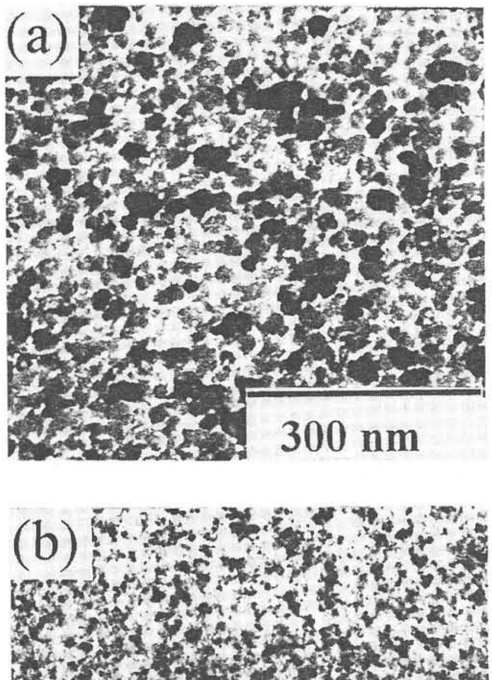

Fig. 1 Planeview TEM micrographs of (a) CVD and (b) PVD TaN films

The XRD results shown in Fig. 2 compare the grain orientation of CVD and PVD TaN films. CVD TaN is highly (200)-oriented, while PVD TaN has (111) preferred orientation. The lattice constants deduced from XRD results for CVD and PVD films are 0.4293nm and 0.4331 nm, respectively. Both are smaller than that of bulk TaN. The carbon and oxygen concentrations in the CVD TaN are 10 at.% and 8 at.% respectively as determined by XPS and AES. XPS results confirm that there is no organic carbon in the CVD film. Caron exists mainly in the form of Ta and C bondings. PVD TaN has no detectable either carbon or oxygen impurities. This may explain why PVD film has a lower resistivity of 380 μΩ-cm as compared to 920 μΩ-cm of CVD film. Both CVD and PVD films have N/Ta ratio of 1.05 to 1.1 from Rutherford backscattering spectroscopy (RBS) analysis.

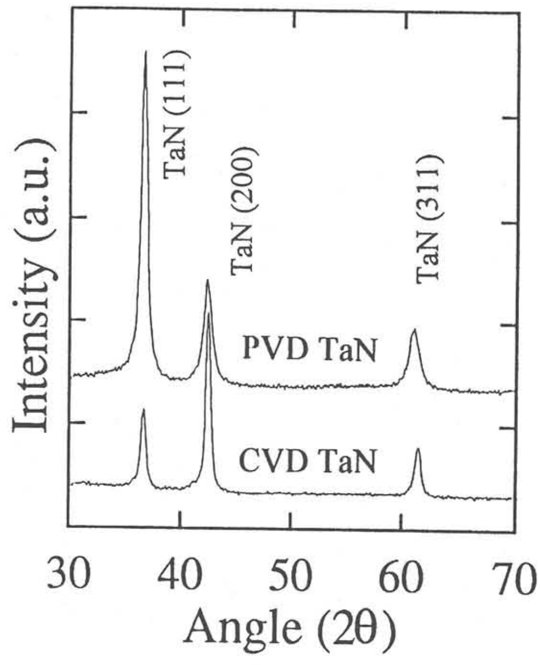

Fig. 2 X-ray diffraction patterns of CVD and PVD films. CVD films show a (200) preferred orientation, while PVD films show a (111) preferred orientation.

In order to evaluate the thermal stability of CVD and PVD TaN as barrier against Cu and Al diffusions, a more sensitive electrical measurement of diode leakage current was employed to detect Cu or Al penetration into the silicon p/n junction regions. The leakage current distribution using CVD TaN in the contact structure Cu(400 nm)/TaN(60 nm)/Si after various temperature annealings is shown in Fig. 3. 42 diodes with an area of 500x500 μm^2 were measured for each annealed sample. The leakage distributions of annealed samples remained the same as those unannealed sample up to 500 °C/30 min annealing. The measurements on the 550 °C-annealed sample show a large portion of leakage current greater than 10-8 A/cm-2. Although TaN and Cu do not react to form compounds at high annealing temperatures, enough copper has diffused through TaN grain boundaries into underlying silicon substrate to cause the failure of junction diode leakage. For comparison, similar evaluations were performed on the diodes using PVD TaN barrier layer. Fig. 4 shows that the leakge distributions remain unchanged up to 550 °C for PVD films. The electrical test results indicate that PVD TaN film has an extra 50 °C temperature margin than CVD film in thermal stability against Cu diffusion.

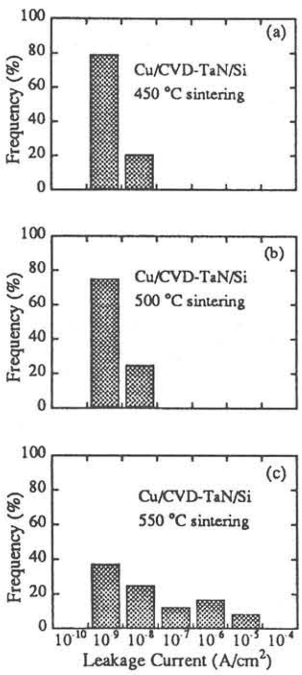

Fig. 3 Diode leakage current distrbution of CVD TaN barrier layer against Cu diffusion after annealing at (a) 450 °C, (b) 500 °C, and (c) 550 °C for 30 min.

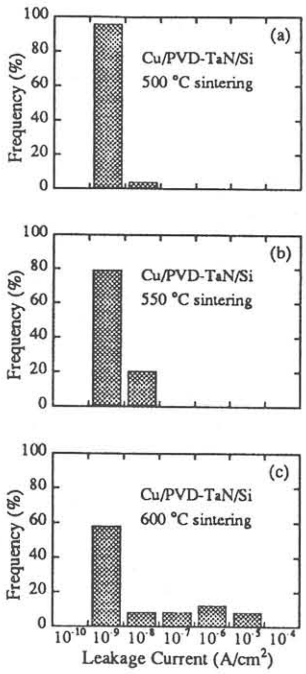

Fig. 4 Diode leakage current distrbution of PVD TaN barrier layer against Cu diffusion after annealing at (a) 500 °C, (b) 550 °C, and (c) 600 °C for 30 min.

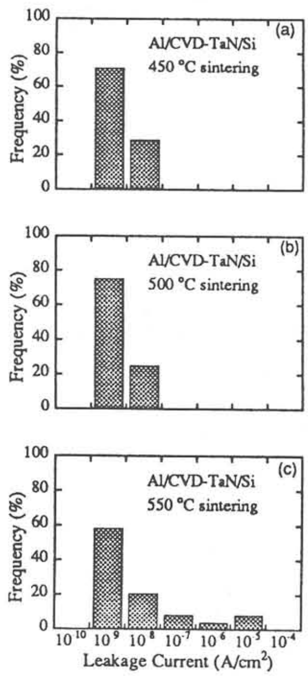

Fig. 5 Diode leakage current distrbution of CVD TaN barrier layer against Al diffusion after annealing at (a) 450 °C, (b) 500 °C, and (c) 550 °C for 30 min.

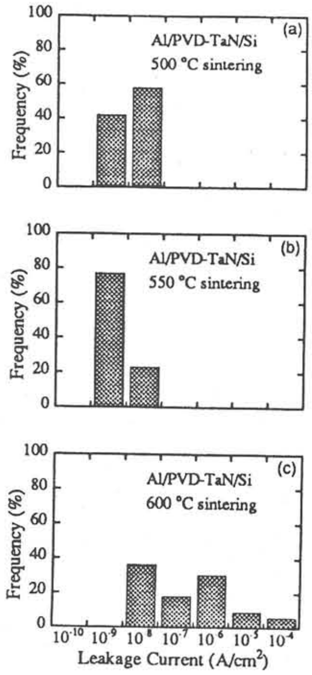

Fig. 6 Diode leakage current distrbution of PVD TaN barrier layer against Al diffusion after annealing at (a) 500 °C, (b) 550 °C, and (c) 600 °C for 30 min.

Fig. 5 shows the diode leakge current distribution of CVD TaN barrier layer against Al diffusion after furnace sintering in N_2 at various temperatures. Similar to Cu diffusion, Al starts to penetrate TaN films around 550 °C. Due to its fine grain structure, PVD TaN also exibits a higher diffusion resistance to Al diffusion as shown in Fig. 6.

IV. CONCLUSION

It has been shown that 60-nm CVD and PVD TaN films are effective diffusion barriers for aluminum and copper interconnections. PVD TaN films can withstand copper diffusion up to 550 °C for 30 min in vacuum without causing p/n junction leakage. CVD TaN has a 50 °C lower thermal stability. This can be attributed to microstructural differences in the two types of films.

ACKNOWLEDGMENT

This work was supported by the National Science Council of the Republic of China under contract NSC84-2215-E009-025 and NSC84-2113-M009-012. We would also like to thank S.H. Chaung for her assistance in CVD TaN deposition.

REFERENCES

[1] M.-A. Nicolet, Thin Solid Films, 52, (1978) 415
[2] M. Wittmer, J. Vac. Sci. Technol. A2 (1984) 273
[3] J. Li, et al., J. Appl. Phys. 72 (1992) 2810
[4] K. Holloway, et al., J. Appl. Phys. 71 (1992) 5433
[5] J.O. Olowolafe, et al., J. Appl. Phys. 72 (1992) 4099
[6] B. Mehrotra and J. Stimmell, J. Vac. Sci. Technol. B5 (1987) 1736
[7] M.A. Farooq, et al., J. Appl. Phys. 70 (1991) 1369
[8] S.C. Sun, et al., Dig. of Symp. on VLSI Technol. (1995) 29
[9] R.M. Fix, et al., Chem. Mater. 5 (1993) 614