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A Comparative Study of CVD and PVD Tungsten Nitride Diffusion Barriers for Cu Metallization

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A comparison of MOCVD tungsten nitride (WN) and PVD WN as diffusion barriers for 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 Cu/WNx/Si contact structures. Results indicate that nitrogen-lean sputtered WNx possesses a higher thermal stability than CVD WNx against Cu diffusion. This is attributed to the sputtered film's ability to resist decomposition from W_2N to α-W. A post-deposition RTN treatment was found to further enhance the thermal stability by about 25 °C.

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. Among them, tungsten nitride has received great interest because it would not form compound with copper [1]. WN deposition can be accomplished through either chemical vapor deposition (CVD) or physical vapor deposition (PVD) method. Previous studies of reactive sputtered WNx have reported that they were excellent metallurgical diffusion barriers between copper and Si [1,2]. 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 [3,4]. Recently we have developed a low-resistivity CVD cubic-phase WN process using a new metalorganic precursor bistertbutylamido-bistertbutylimido-tungsten (BTBTW) [5]. The thermal decomposition process has the advantage of good step coverage and avoiding particle contamination from gas phase reaction. A post deposition rapid thermal annealing in NH_3 (RTN) was attempted to further enhance the thermal stability.

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

II. EXPERIMENTAL

The deposition of CVD WNx film was carried out in a cold-wall, low-pressure CVD reactor at substrate temperature of 500 °C. The base pressure was maintained at 1x 10^{-5} torr by a diffusion pump. Argon was used as

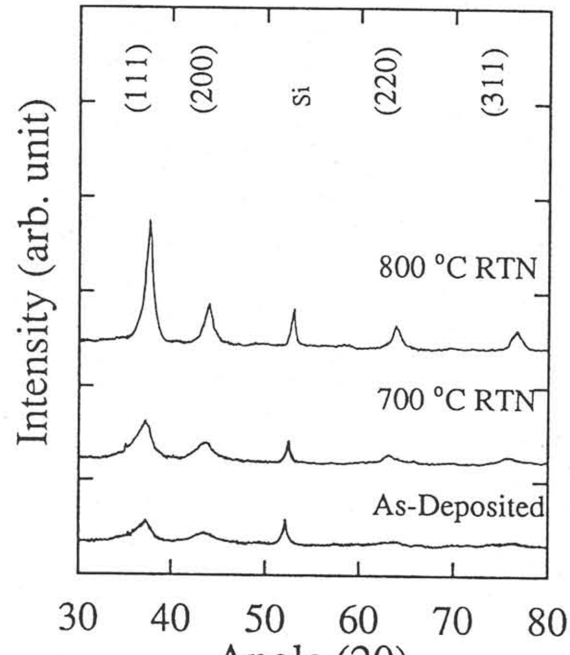

Fig. 1 X-ray diffraction patterns of CVD WNx of the as-deposted and RTN annealed films.

the carrier gas at a flow rate of 40 cm^3 min^{-1} to carry the vapor of BTBTW into the reaction chamber. 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 pressure of 20 mtorr.

PVD films were deposited by reactive sputtering of W target in a gas mixture of argon to nitrogen ratio equal to 12/3, 12/4 and 12/6 at a pressure of 8 mtorr. The base pressure was maintained at $1x10^{-6}$ torr. The samples were exposed to the air before 400 nm copper 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), and wavelength dispersive spectroscopy (WDS). Interdiffusions of Cu and Si in the WNx 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).

Contact structure of Cu/WNx/Si of p^+n junction diodes used in the electrical evaluation. Junctions were first formed by impanting BF_2^+ at 50 KeV and a dose of $3x10^{15}$ cm^{-2}. The samples were annealed at 900 °C for 30 min in nitrogen. WNx barrier layers were subsequently deposited in the contact structures using either CVD or PVD technique. 400 nm-Cu was sputtered on top of 50-nm WNx films. WNx was etched by SF_6 plasma after Cu patterns were defined. Samples were then thermally annealed at temperatures ranging from 400 to 600 °C in N_2. The leakage current was measured using HP4145B at 5V reverse bias for thermal stability study. RTN was performed at 700 °C for 60 sec.

III. RESULTS AND DISCUSSION

Fig. 1 (a) shows the XRD patterns of CVD WNx before and after RTN treatment. The lattice constant of the as-deposited CVD WNx is 0.4175-nm which is larger than 0.4127-nm of β-W_2N. The N/W ratio from WDS measurement is 1.7, indicating that the CVD film is nitrogen rich. This may explain why the CVD film has high resistivity (4500 $\mu\Omega$-cm). After RTN treatment the resistivity is reduced to about 1200 $\mu\Omega$-cm. This may be attributed to a reduction in the carbon content, growth in grain size through polycrystalline recrystallization, as well as the increase in film density.

The thermal stability against Cu diffusion was examined by using p^+n junction diode leakage current measurement. The distribution of of the leakage current density remains below $1x10^{-8}$ A/cm^2 for those samples annealed at temperatures up to 500 °C for 30 min in N_2

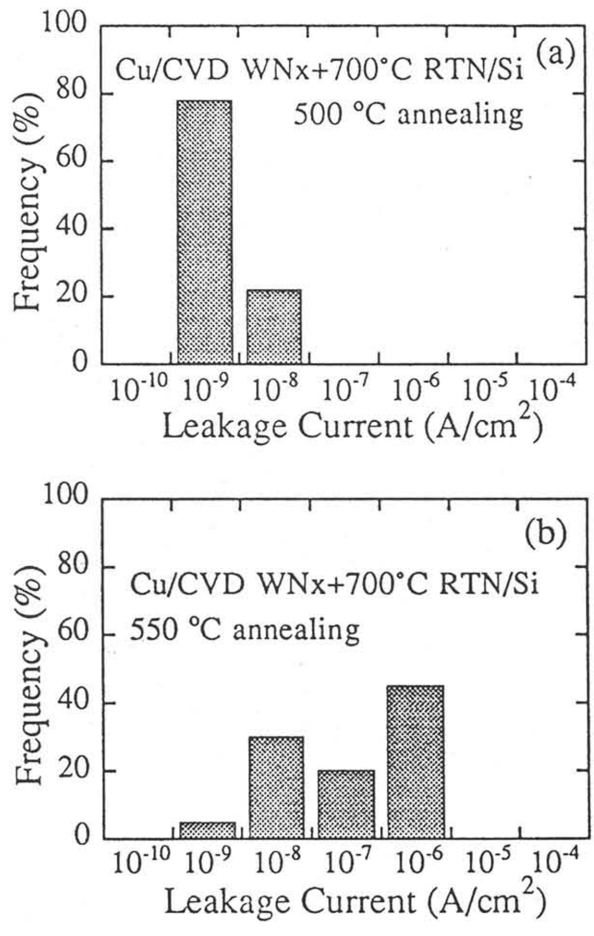

Fig. 2 Diode leakage current distrbution of CVD WN barrier layer against Cu diffusion after annealing at (a) 500 °C, and (b) 550 °C.

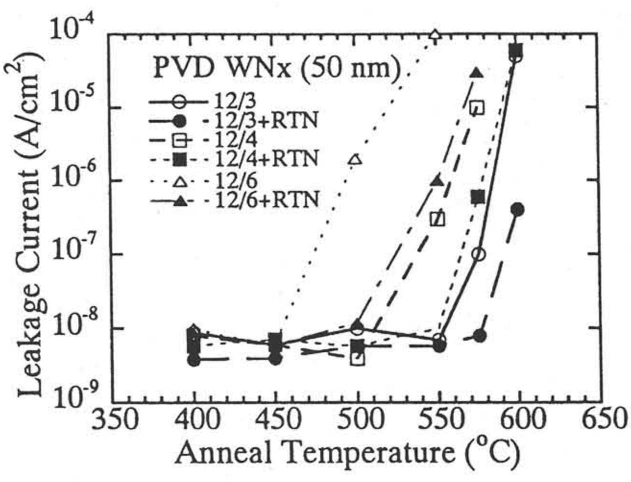

Fig. 3 Diode leakage current distrbution of PVD WN barrier layer against Cu diffusion as a function of annealing temperature.

ambient. Fig. 2 shows the diode leakge current distribution of 700 °C-RTN CVD WNx barrier layer after annealed at 500 and 550 °C for 30 min, respectively. RTN treatment has improved the thermal stability by about 25 °C.

Fig. 3 shows the results of thermal stability of PVD WNx with and without RTN against Cu diffusion. Nitrogen-lean film had a higher thermal stability than nitrogen-rich film. Several reasons were proposed to explain this phenomenon. The amorphous nitrogen-lean film is lacking the fast diffusion path in the structure. Another possibility is that the nitrogen-lean film was more resistant to the loss of nitrogen during high-temperature processes. The RTN treatment has improved the thermal stability of the 12/3 film by 25 °C.

Fig. 4 shows the SIMS depth profiles of Cu/WNx/p+n Si structures with 12/3, 12/4, and 12/6 WNx barrier annealed at 575 °C. After 575 °C annealing, a peak of Cu signal was found at the interface of 12/3 WNx and Si interface. The Cu signal is still far from the junction region. The I-V data confirm that this is a good diode. For 12/4 WNx barrier, the Cu signal extended deeply into the junction region and caused a high reverse leakage current. Similar results were observed for 12/6 films.

IV. CONCLUSION

It has been shown that 50-nm CVD and PVD WNx films are effective diffusion barriers for copper interconnections. Nitrogen-lean PVD WNx films can withstand copper diffusion up to 550 °C for 30 min in N_2 without causing p/n junction leakage. CVD TaN has a 50 °C lower thermal stability. This is attributed to the sputtered film's ability to resist decomposition from W_2N to α-W. A post-deposition RTN treatment was found to enhance the thermal stability by about 25 °C.

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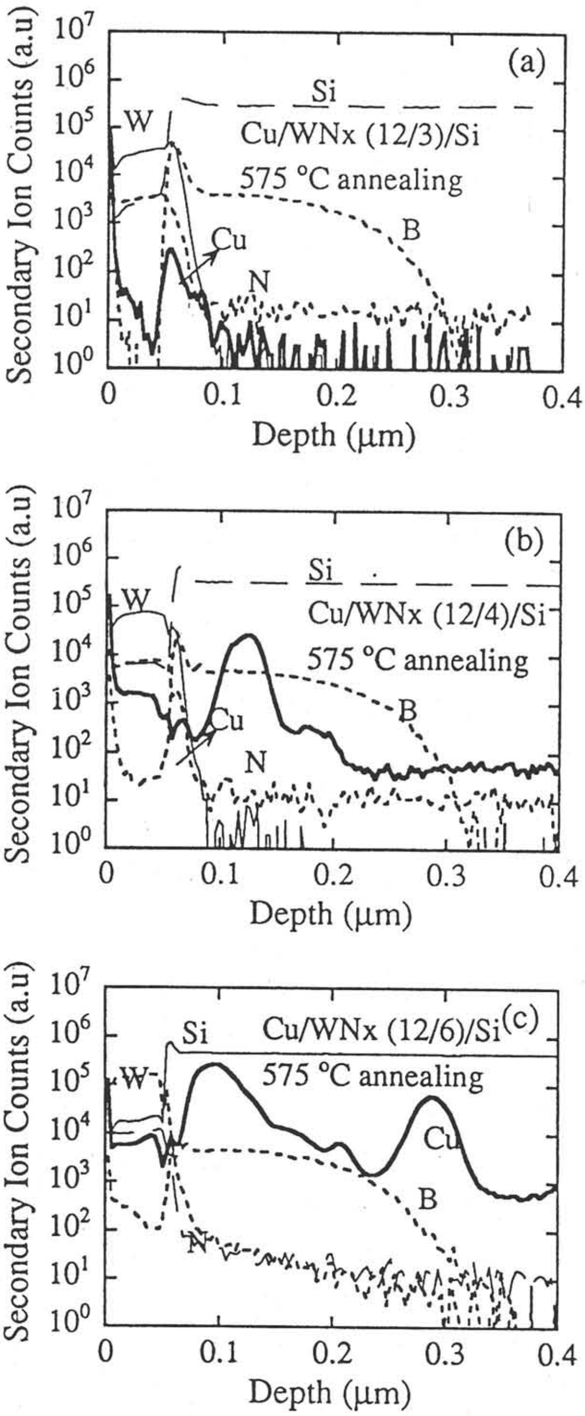

Fig. 4 SIMS depth profiles of (a) 12/3, (b) 12/4, and (c) 12/6 WNx samples after 575 °C annealing.