Titanium Nitride Diffusion Barriers and Schottky Diodes

Andrew Woodard
Microelectronic Engineering
Rochester Institute of Technology
Rochester, NY 14623

Abstract-**Titanium nitride was studied for use in two applications: as a barrier metal in an aluminum metallization and as a Schottky diode metal on n-type silicon($N_D = 1x10^{15}/cm^3$). The films were reactively sputtered in an RF magnetron configuration using a Perkin-Elmer 2400 sputtering system. Effects of heat treatment temperature on performance were studied for both applications. TiN as sputtered in this experiment was shown to be an effective barrier against Al-Si interdiffusion. Annealing temperature was shown to affect the Schottky barrier height, which ranged from 471 to 658 mV as calculated from specific contact resistivity.**

I. INTRODUCTION

Necessity of Diffusion Barriers

THE simplest method for connecting transistors in MOS integrated circuits is by direct application of a contiguous aluminum film to two or more source/drain regions. Unless the IC is kept away from oxygen between contact etching and aluminum deposition, there will be a native SiO_2 between the semiconductor and the interconnect. This is generally removed through sintering, a heat treatment in which the native oxide dissolves in the aluminum, allowing intimate contact between metal and semiconductor.

Once the oxide is dissolved, a phase boundary between Al and Si is created. At typical sintering temperatures (425 to 450°C), Si is quite soluble in Al, and it begins to migrate into the interconnect. The displaced Si is replaced by the nearest available substance, Al. Si migration does not happen uniformly. Rather, Si atoms migrate preferentially from isolated surface defects such as dislocations. Therefore, aluminum invades these locations almost exclusively. The depth of penetration of Al spikes can be significant, on the order of a full micron or more depending on time and temperature of the treatment.

As CMOS is scaled to lower power, shorter channels, and higher clock frequencies, drain-well junctions must be as shallow as possible. Al spikes can short drain-well junctions if allowed to pass the junction depth. Preventing Si from entering the interconnect is therefore of utmost importance. One strategy proposed to combat this problem is pre-saturating the interconnect with silicon to remove the concentration gradient that drives diffusion. However, the solid solubility increases during sintering, and the extra Si that enters the interconnect precipitates out upon cooling, interfering with current pathways. Current crowding and electromigration can result, causing premature failure. A conductive physical barrier is therefore the best way to control interdiffusion and spiking.

Schottky Diode Principles

When a metallic material is placed in contact with a semiconductor whose doping level is less than about $10^{17}/cm^3$, the I/V characteristic of the interface resembles that of a p/n junction with a few notable differences. First, the current is virtually all majority carrier current, and secondly, the voltage drop is typically less than that of a pn junction. Thus, when polarity is changed, there is no long delay while minority carriers are recombining.[1] Put in parallel with the base-collector junction , a Schottky diode can act as a short preventing the junction from entering saturation. The transistor can then switch much more rapidly, and this is the basis for Schottky-TTL circuits.

Current flow in a Schottky diode is predicted by the expression

$$J = A^{**}T^2 e^{-q\phi_B/kT} \times (e^{qV/kT} - 1)$$

where A** is Richardson's constant (120 A/cm^2K^2) and ϕ_B is the barrier height between the Fermi level and the conduction band at the semiconductor surface. Near zero bias, the specific contact resistance is given by

$$R_c = {}^{dV}/_{dJ} = ({}^{k}/_{qA^{**}T})e^{q\phi_B/kT}$$

It can be seen that the barrier height can be extracted directly from the reciprocal tangent slope of the I/V curve at zero bias. This is the method chosen to determine barrier height in this experiment.

II. EXPERIMENTATION AND RESULTS

The objectives of the experiment were to observe deposition rate and resistivity of sputtered TiN films, pattern TiN by wet and dry techniques, determine the effect of barrier presence and sinter temperature on Al spiking, and measure Schottky barrier height of the TiN:Si contact.

Sputtering TiN

All sputtering was carried out in a Perkin-Elmer 2400 RF magnetron system with an 8" Ti target. The sputtering ambient consisted of 22.5 sccm Ar and 7.5 sccm N_2 at a chamber pressure of 5 millitorr. At 500 Watts of forward power, the sputter rate was 300 Å per hour in table rotation mode and 2400 Å per hour in stationary mode(the 8" Ti target covers 45 degrees of table rotation at a radial position of 10 inches). Thickness was measured using a Tencor AlphaStep™ profilometer. Steps were generated by placing fragments of wafers on glass slides as shadow masks. The resulting film had both a step and an insulating substrate, making it ideal for both profilometry and sheet resistance measurement.

Sheet resistance was measured by four point probe. The sheet resistance is given by

$$R_s = f_1 (V / I)$$

where I is the current passed between the outer two probes and V is the voltage observed between the inner two probes. For infinitely wide wafers, the geometric correction factor is $\pi/\ln 2$, or 4.532. The area of the film I measured could be likened to the area of a 2" wafer, and for this case the correction factor (based on ratio of wafer diameter to probe spacing) is 4.493. The resistivity values obtained for the films ranged from 400 to 650 $\mu\Omega$-cm. This is about one order of magnitude greater than the 55 $\mu\Omega$-cm reported by Wittmer, et al.[2] However, Wittmer sputtered at 1000 W, 1 mtorr, and a 12:1 Ar/N_2 ratio, and his tool had a base pressure of 2×10^{-7} torr. The sputterer in use for this experiment could only draw a 2 μtorr vacuum, and the maximum safe power rating is 500 W.

Pattern Definition

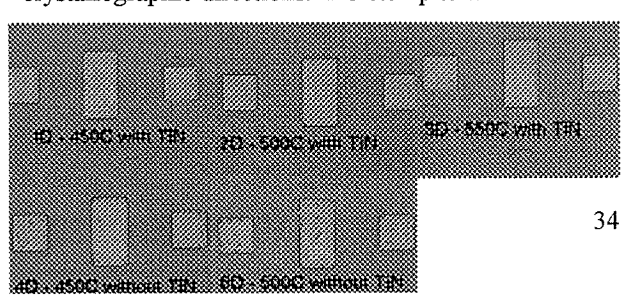
A solution of 5 parts DI water, 5 parts H_2O_2, and one part ammonium hydroxide heated to 75°C has been demonstrated to strip TiN.[3] However, this same mixture attacks photoresist aggressively, so a bilayer mask was investigated. 2000 Å of Al was evaporated over 600Å of TiN on wafers which were then painted with photoresist stripes and hardbaked. Phosphoric acid at 50°C was used to pattern the Al. TiN was unaffected by this. Photoresist was dissolved in acetone leaving Al stripes over TiN. The TiN etch solution removed the 500Å in 45 seconds, and the Al layer succeeded as an etch mask. Stripping the etch mask in Al etch left TiN where the original photoresist had been. This process, though demonstrated to be possible, was not evaluated for small geometries, and the bilayer scheme adds time and complexity to the processing of a lithographic layer. A plasma process had to be investigated as an alternative.

Many transition metal and refractory metal fluorides are volatile, so fluorine-based chemistry is a logical choice for plasma etching transition nitrides. In the RIT IC factory, silicon nitride is etched with SF_6 at 300 millitorr and 50 Watts of RF power. SF_6 flow rate is typically set at 30 sccm. This process etched TiN-coated wafers bare with good radial uniformity. The endpoint is detected when the lavender color of TiN etching turns white and gives way to the sky blue color of SF_6 attacking Si underneath. Selectivity over Si is likely poor, but with such a thin TiN layer, damage to Si is minimized. This dry etch process was used to pattern the actual Schottky diodes.

Sintering Experiment

Spiking tests were carried out to evaluate diffusion barrier performance. First, 6 wafers were oxidized in wet O_2 at 1050°C to a thickness of 1 μm. 20μm contact holes were etched down to the substrate using standard photolithography and buffered HF. Immediately prior to TiN sputtering, the wafers were cleaned again in dilute 50:1 HF and dried without DI water rinse. 600 Å of TiN was deposited on three of the wafers followed by 4000 Å of Al on all 6 to complete the metallization. Thirty minute sinters in forming gas at 450°, 500°, and 550°C were performed with one Al-Si stack and one Al-TiN-Si stack in each run. The only exception is the lack of an Al-Si stack at 550°C. A eutectic reaction exists at 577°C in the Al:Si binary system, and the formation of a liquid phase inside the furnace was to be avoided. Temperature setpoint control of the equipment used is such that the risk of a 25° overshoot was real. Thus the hottest run for the unprotected contact was omitted.

After sintering, the metallization was stripped one layer at a time: Al in 50°C H_3PO_4 and TiN in 75°C 5:5:1 $H_2O:H_2O_2:NH_4OH$. The Si surface left behind was inspected optically at 50x for the presence of rectangular etch pits indicating Al migration along crystallographic directions. No etch pits were found on



wafers having the TiN barrier. Etch pits occurred on both Al-Si direct contacts, and their size and number increased with sinter temperature. Thus 600Å of TiN

Figure 1: Spiking tests showing effect of TiN barrier

was shown to prevent spiking over the time and temperature range of this experiment. Photos of the stripped contacts can be seen in Figure 1. It is unclear whether the barrier was sacrificial in nature or not since it was not stressed to failure. However, previous work has indicated that TiN is eventually consumed when not accompanied by a silicide contact layer.[3]

Schottky Diode Fabrication/Testing

The starting substrates were n-type with doping approximately $10^{15}/cm^3$. An ohmic n+ contact was formed on the back of 6 wafers via arsenic predeposition. With the n+ layer in place, the substrates were RCA cleaned followed by a dip in 50:1 diluted HF solution. From there the wafers were spin dried (no rinse) and transferred immediately to the sputtering equipment for 600Å TiN deposition. Following sputtering, half hour anneals in forming gas were carried out at 450, 500, 550, and 600°C, one wafer per anneal. A control wafer received no heat treatment. The annealing brought about two changes in the films. The first noticeable change was in color, depending on temperature. With increasing anneal temperature, the film became salmon pink, then deep magenta, then yellow-green. The same observation was made by Clarke,[4] and he attributes this to changes in composition. The gold color corresponds to 1:1 Ti:N stoichiometry, and nitrogen enrichment produces the deep magenta color. The added nitrogen could only have come from the ambient forming gas inside the furnace. Besides color change, the anneal temperature affected barrier height. Figure 2 shows the observed barrier height as a function of anneal temperature.

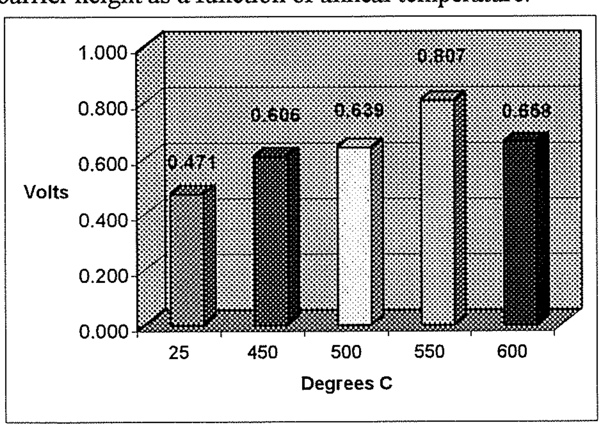


Figure 2: Observed barrier height as a function of anneal temperature

Reverse leakage current was reduced by annealing. The 550° case does not fit the trend because of excess resistance due to surface contamination originating in the photolithographic patterning of the diodes.

III. CONCLUSION

The barrier height measurement method chosen was done so for its simplicity and ease rather than for accuracy. C/V analysis could yield more accurate values, especially since it can account for diode ideality and series resistance of the film and bulk substrate. Experimentation with sputtering conditions could produce a faster process and less resistive films. Annealing in hydrogen without nitrogen could help avoid nitrogen enrichment if the as-sputtered stoichiometry is desired. Quantitative evaluation of diffusion barrier performance by RBS would provide more insight into failure mechanisms and the importance of different film properties in diffusion prevention.

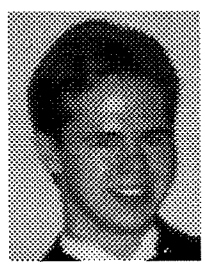
REFERENCES

[1] W. R. Runyan and K. E. Bean, *Semiconductor Integrated Circuit Processing Technology*, New York: Addison-Wesley 1990.

[2] M. Wittmer, "Electrical Characterization of Reactively Sputtered TiN Films," *J. Appl. Phys.* **52**, 5722 (1981).

[3] H. Joswig and W. Pamler, "Stoichiometry Effects in TiN Diffusion Barriers," *Thin Solid Films* **221**, 228 (1992).

[4] P. J. Clarke, "Magnetron dc reactive sputtering of titanium nitride and indium-tin oxide," *J. Vac. Sci. Tech.* **14**, 141 (1977).



Andrew Woodard, originally from Fort Worth, Texas, received a B.S. in Microelectronic Engineering from the Rochester Institute of Technology in 1998. He is currently pursuing an M.S. in Materials Science and Engineering from RIT. Andrew has been active in Tau Beta Pi's NY Π chapter since 1997 and received a Student Commencement Speaker nomination in his graduating year.