STUFFED NO LAYER AS A DIFFUSION BARRIER IN METALLIZATIONS FOR HIGH TEMPERATURE ELECTRONICS

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Abstract

Auger electron spectroscopy (AES) was employed to characterize the diffusion barrier properties of molybdenum in the CrSi2/Mo/Au metallization system. The barrier action of Mo was demonstrated to persist even after 2000 hours annealing time at 300°C in a nitrogen ambient.

At 340°C annealing temperature, however, rapid interdiffusion was observed to have occurred between the various metal layers after only 261 hours.

At 450°C, the metallization degraded after only two hours of annealing.

The presence of controlled amounts of oxygen in the Mo layer is believed to be responsible for suppressing the short circuit interdiffusion between the thin film layers. Above 340°C, it is believed that the increase in the oxygen biblity led to deterioration of its stuffing action, resulting in the rapid interdiffusion of the thin film layers along grain boundaries.

The CrSi₂/Mo/Au barrier metallization system lent itself easily to fine line patterning.

Introduction

Thin film metallizations play a critical role in the reliability of microelectronic devices. The deleterious effects of aluminum alloy penetration 1-2 and the "purple plague" 3-4 in gold-aluminum thin film couples are well-known examples. Thin film metallizations are made up of very small grains, high densities of grain boundaries and dislocations. It is well established that grain boundaries and dislocations increase atomic mobility by acting as short circuit diffusion paths. $^{5-6}$. Gjostein 6 has shown that for face centered cubic metals, thin film interdiffusion is controlled by dislocation pipe diffusion and grain boundary diffusion in the temperature range 30-60 percent of the melting point. Below this temperature range, interdiffusion is not very significant. Above this temperature range, lattice diffusion predominates. Diffusion barriers, such as stuffed barriers, passive barriers, sacrificial parriers and thermodynamically stable barriers, are intended to suppress short circuit controlled interdiffusion. The purple plague mentioned earlier can be ascribed to Kirkendall voiding through short circuit interdiffusion.

Harris et al 8 reported that the diffusion of Ti in Mo was inhibited by the presence of oxygen in the Mo layer of a Ti/Mo/Au system. Nowicki and Wang observed the suppression of Au-Si intermixing in Si/Mo/Au system if the Mo layer was reactively sputtered in N2-Ar mixture. They attributed the enhanced Mo barrier action to N2 occupation of the octahedral sites around the Mo atoms. Neither of the above studies dealt with prolonged annealing effects at high temperatures.

The need for high temperature (up to 300°C) micro-electronics applications in such diverse fields as aircraft engine controls, nuclear reactor core monitoring instrumentation and oil and gas well downhole instrumentation has further imposed stringent reliability requirements on microelectronic interconnections. Diffusion barrier protection of the ohmic contact layer and metal conductor layer thus assumes new importance. This paper will discuss the enha.med high temperature diffusion barrier properties achieved through the introduction of controlled amounts of oxygen in the Mo barrier layer of the Cr/Mo/Au metallizat.on system.

A barrier metallization system is shown schematically in Figure 1. It consists of an ohmic contact layer (CrSi₂), a diffusion barrier layer (stuffed Mo) and an interconnect or conductor layer (Au). Figure 2 illustrates a tri-metal system where diffusion barrier protection is lost during heat treatment.

Experimental Procedure

Sequential deposition of the thin film layers of Cr, Mo, and Au on (111)-oriented, N-type silicon single crystal wafers was carried out using planar r.f. magnetron sputtering (Perkin-Elmer Ultec Model 2400-85A). Sputtering pressures were less than 10 mtorr using argen. Oxygen-argon gas mixtures were utilized for reactive sputtering of the Mo. Prior to sputtering, the silicon wafers were etched in dilute HF, rinsed thoroughly in de-ionized water, air dried and transferred immediately into the sputtering chamber.

After sequentially depositing the Cr/Mo/Au system, sintering was performed in a quartz tube in a flowing nitrogen ambient at 450°C for 15 minutes to affect CrSi₂ formation.

Annealing experiments were subsequently carried out at 300°C, 340°C and 450°C. The 300°C anneals were performed in nitrogen ambients in a quartz tube for 168 hours, 1000 hours and 2000 hours.

Annealing experiments above 300°C were carried out in vacuum. ACS was employed to study the extent of thin film interdiffusion between the various metal layers. Fine line pattern definition was evaluated using a combination of pnotolithographic and chemical etching techniques.

Results and Discussions

AES profiles of the Cr/Mo/Au system before and after sintering at 300°C are shown in Figures 3-6. There was limited penetration of the Cr layer by the Mo layer during the sputter deposition. After annealing at 300°C for 2000 hours, the diffusion barrier properties of the Mo layer were found to be intact. Some redistribution of the oxygen in the Mo layer occurred during the 300°C annealing. The suppression of the expected grain boundary interdiffusion may be



ascribed to the oxygen incorporated into the Mo layer. The stuffing behavior of oxygen may be similar to that of nitrogen in Ti-W observed by Nowicki et al¹⁰ in the Al/Ti-W/Au system. Nowicki and Wang also reported that controlled incorporation of nitrogen into molybdenum significantly reduced the rate of grain boundary interdiffusion in Mo/Au couples.

Annealing above 300°C revealed that oxygen stuffing does not completely suppress short circuit controlled interdiffusion such as shown in the AES profile of Figures 7 and 8. In fact, at 450°C, the oxygen mobility was so high that stuffing action was lost with a resultant loss of Mo barrier action after only 2 hours of annealing. This observation is consistent with the equations of Gjostein⁶ and other recently observed thin film interdiffusion phenomena⁶. Fine line patterning was accomplished using photolithography and chemical etching such as shown in Figure 9. The fine lines are two microns in width.

Summary

The diffusion barrier action of stuffed Mo layers has been demonstrated to be reliable at 300°C for at least 2000 hours in a nitrogen ambient. The incorporation of oxygen in the Mo layer is believed to be responsible for the enhanced diffusion barrier action of the Cr/Mo/Au metallization system at temperatures below 300°C. Above 300°C, the Mo barrier action rapidly deteriorates.

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List of References

- 1. C. J. Santoro, J. Electrochem. Soc. 116 361-364 (1969).
- R. Rosenberg, J. J. Sullivan and J. K. Howard in Thin Films-Interdiffusion and Reactions edited by J. M. Poate, K. N. Tu and
- J. W. Mayer (John Wiley and Sons, NY, 1978). J. F. E. Baglin and J. M. Poate, ibid. J. A. Cunningham, Solid State Electron, 8 735 (1965).
- R. W. Balluffi and J. M. Blakely, Thin Solid
- Films, 25, 363-392 (1975). 6. N. A. Gjostein, in Diffusion, Am. Soc. Metals,
- Metals Park, Ohio, 1973, pg 241.
 7. M. A. Nicolet, Diffusion Barriers in Thin Films,
- Thin Solid Films, 52, 415-443, 1978.

 J. M. Harris, E. Lugujjo, S. U. Campisano,
 M. A. Nicolet and R. Shima, J. Va. Sci.
- Technol. 12 (1), 524-527 (1978).
 R. S. Nowicki and I. Wang, J. Vac. Sci. Technol.,
- (2), 235-237, (1978).
 R. S. Nowicki, J. M. Harris, M. A. Nicolet and I. V. Mitchell, Thin Solid Films, <u>53</u>, 195-205 (1978).

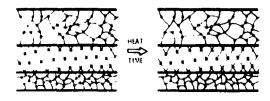


Figure 1: SCHEMATIC RELIGITRATION OF A STUFFED BARRIER NOTE THE ASE OS INFORMATION SECREMATES TO GRAIN HOUNDARIES

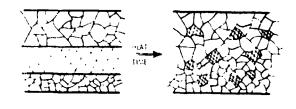


Figure 2: Indivate his stration of a tri metal system affect barries on the front is lost distributed the attent to a free the control of the

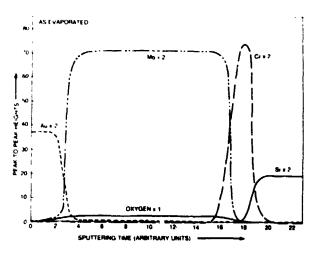


Figure 3: AES SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTER CrSi2 FORMATION

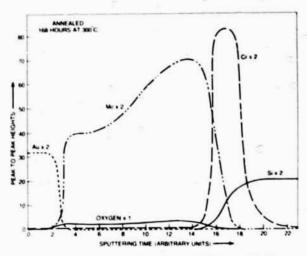


Figure 4: AES SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTER A 168 HOUR ANNEAL AT 300°C FOLLOWING THE CrSi₂ FORMATION

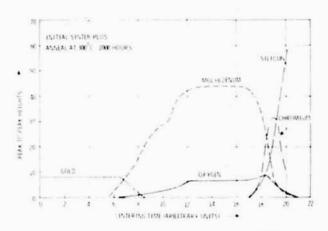


Figure 5: AES SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTER A 1000 HOUR ANNEAL AT 300°C FOLLOWING THE CrSi₂ FORMATION

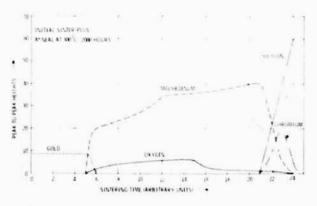


Figure 6: AES SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTER A 2000 HOUR ANNEAL AT 300°C FOLLOWING THE CrSi₂ FORMATION

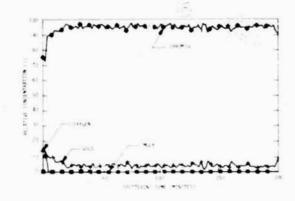


Figure 8: ACS SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTER VACUUM SINTERING AT 450°C FOR 2 HOURS



Figure 9: PHOTOMICROGRAPH OF FINE LINE PATTERNING OF THE Cr/Mo/Au SYSTEM. THE FINE LINES ARE 2 MICRONS IN WIDTH.

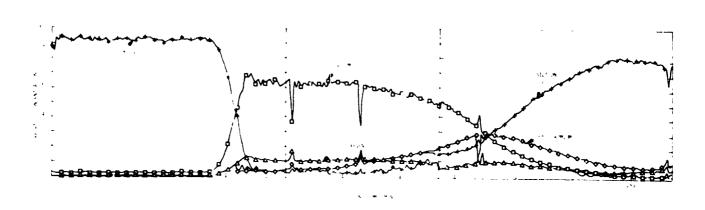


Figure 7: AES SPUTTER PROFILE OF THE Cr/Mo/Au SYSTEM AFTEP VACUUM SINTERING AT 340°C FOR 264 HOURS