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EFFECTS OF DIFFUSION ON INTERFACIAL FRACTURE OF MULTILAYER HYBRID MICROCIRCUIT FILMS

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ABSTRACT

In this study, the effect of diffusion on gold-chromium film durability was determined from interfacial fracture energy measurements on laboratory samples aged to simulate long term service. The samples were prepared by sputter deposition of gold films and chromium adhesive layers on sapphire substrates. Some films were left in the as-deposited condition while others were given an accelerated age to drive the chromium off the interface. Stressed overlayers and nanoindentation were then used to induce interfacial delamination and blister formation from which interfacial fracture energies were determined using mechanics-based models. The results clearly showed that diffusion-induced changes in composition and structure of the films markedly alter susceptibility to interfacial fracture.

KEYWORDS: Gold films, gold-chromium films, stressed overlayers, nanoindentation, interfacial fracture

INTRODUCTION

Interface structure and composition are two of the most important factors controlling the performance and reliability of thin film devices [1,2]. They are particularly important in gold-chromium hybrid microcircuits which consist of an alumina substrate, a thin chromium layer for adherence, and a gold layer for conductance to connect components on the microcircuit [3-5]. During post deposition annealing, lead-frame bonding and service at elevated temperature, diffusion and segregation change the composition and structure of the films and interfaces [3-7]. This has caused significant concern as to the long-term effects of chromium migration on film performance and durability and has motivated numerous studies on diffusion processes and their effects on film properties and performance. These tests have repeatedly shown that chromium diffusion continues until the chromium adhesion layer has been depleted. Nevertheless, the effect of these changes on film adhesion is not well defined due to limitations in quantitative test and analysis techniques [8-10]. These measurements are made even more difficult for ductile films where extensive plasticity limits the stress that can be applied at the film-substrate interface [8]. Recent work by Kriese and coworkers [8,10] following earlier work of Bagchi et al. [11,12] shows that this limitation can be overcome by deposition of a hard highly stressed overlayer. This overlayer applies a uniform stress to the ductile films while constraining out-of-plane plasticity [11-13]. We used this approach to study how changes in composition and structure of gold-chromium films affect susceptibility to interfacial fracture. The results clearly show that chromium promotes adhesion. More interestingly, the strong increase in fracture resistance observed accompanying chromium layer depletion suggests that the relationship between interface structure and deformation dictates film performance.

MATERIALS AND PROCEDURE

In this study, thin gold and gold-on-chromium films were sputter deposited onto polished single crystal (0001) sapphire. Deposition began by heating the substrates to 700˚C in vacuum to drive off moisture followed by a cool to room temperature. The films were deposited on the substrates using chromium and gold targets and argon as the carrier gas. Chromium was deposited first to a thickness of 6 nm. This was followed by gold deposition to a thickness of 200 nm. A gold-on-sapphire film was created for reference.

The gold-on-chromium film samples were then divided into three groups. One group was left in the as-deposited condition. A second group was heated at 400˚C for 2 hours in air at which point chromium had begun to come off the sapphire interface in many regions. The third group was then heated at 400˚C for 8 hours in air after which all the chromium had migrated off the interface. During heating, chromium diffused through the gold to the surface leading to Cr_2O_3 formation upon exposure to air. This oxide was removed using a solution of ceric ammonium nitrate prior to any subsequent fabrication or testing process.

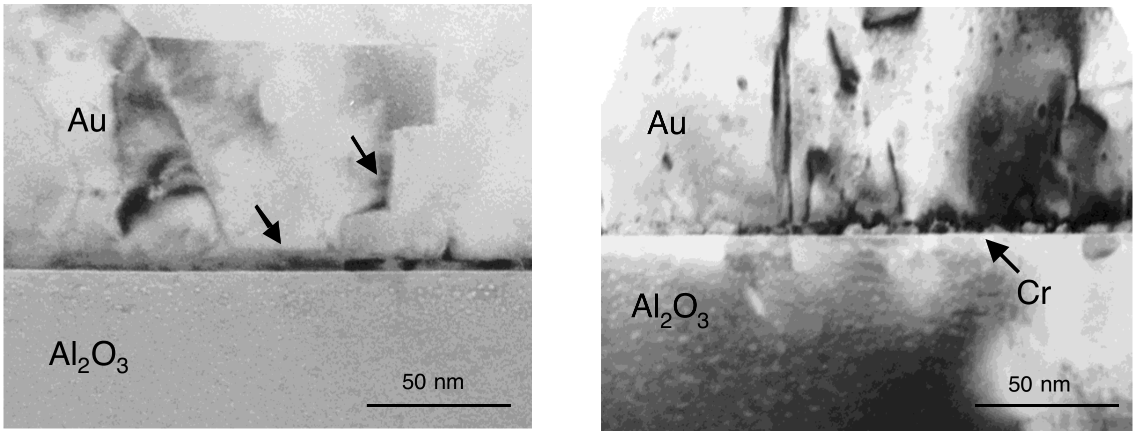
Mechanical properties were determined for each film system using the continuous stiffness option on a Nano Indenter II™ and a Berkovich diamond indenter. All measurements were conducted at an excitation frequency of 45 Hz and displacement of 3 nm. Following nanoindentation, tantalum nitride (Ta_2N) overlayers were deposited on all films to provide a uniform compressive stress for fracture testing. These films were deposited using a tantalum target, argon as a carrier gas, and controlled additions of nitrogen. 450 nm-thick Ta_2N overlayers were sputtered on the gold-on-chromium films. An overlayer 275 nm thick was deposited on an as-deposited gold film to explore the minimal stress needed to cause buckling when chromium was not present.

RESULTS AND DISCUSSION

Structure

The structure and composition of the films were determined using x-ray diffraction and Transmission Electron and Scanning Auger Microscopy. Figure 1 shows that the as-deposited gold and gold-chromium films formed fine scale structures along the substrate interfaces. In the gold films the structure was characterized by formation of 5-nm-thick (111) interface twins parallel with the substrate interface. Continued deposition led to extensive through thickness twinning. In the gold-chromium films, the 5-nm-thick chromium adhesive layer formed the fine scale structure. No long interface twins formed in the gold on the chromium but extensive through thickness twinning did occur within the gold film.

Scanning Auger Microscopy of the films showed a well-defined chromium peak at the interface with the sapphire substrate corresponding to the chromium adhesive layer. (Figure 2.) Aging at 400˚C for 2 hours led to through thickness migration of chromium and partial depletion of the adhesive layer. This was confirmed by backside optical examination where a thin translucent chromium layer covered the substrate interface. In contrast, long term annealing led to complete depletion of the chromium adhesive layer creating a uniform through thickness gold-chromium solid solution. Backside optical examination did not reveal any evidence of a chromium interlayer. The structure and stresses within the tantalum nitride overlayers were characterized using a Rigaku X-ray diffraction (XRD) system with a thin film detection system and Cu-Kα radiation. The patterns showed a randomly oriented polycrystalline structure for these overlayers, typical for sputter-



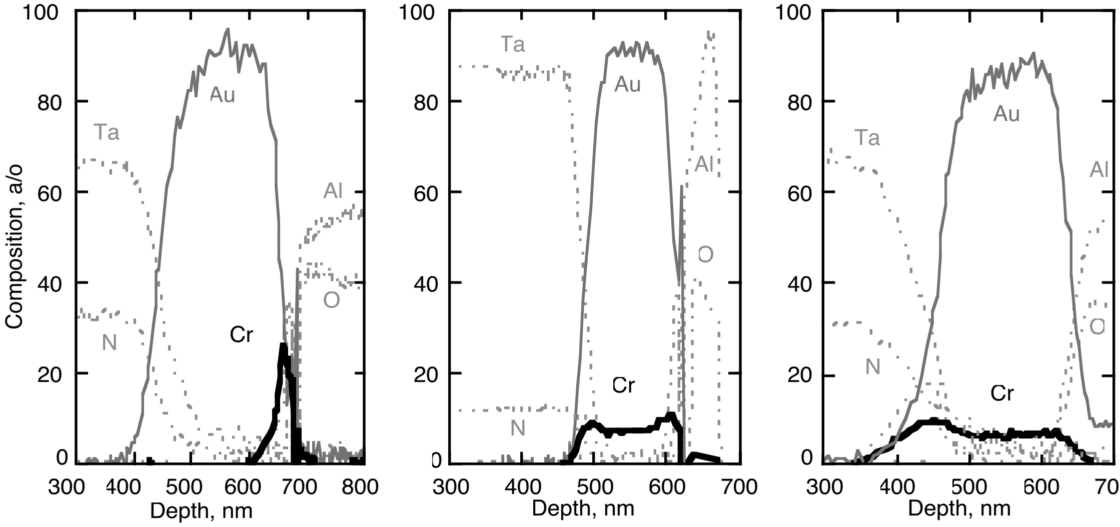
(a) (b)

Figure 1. (a) Interface twins formed in the gold along the sapphire substrate during deposition. Continued deposition led to extensive through thickness twinning. (b) Only through thickness twins formed in the gold on chromium films during deposition.

deposited tantalum nitride. Out-of-plane strain, indicated by shifts in the 2θ peak position for (101), (110), and (211) planes, was then used to calculate the in-plane residual stress assuming isotropic elasticity [14-16]. This gave a compressive stress value of 2.5 GPa which was subsequently confirmed using an inclined angle method for measuring residual stress [16].

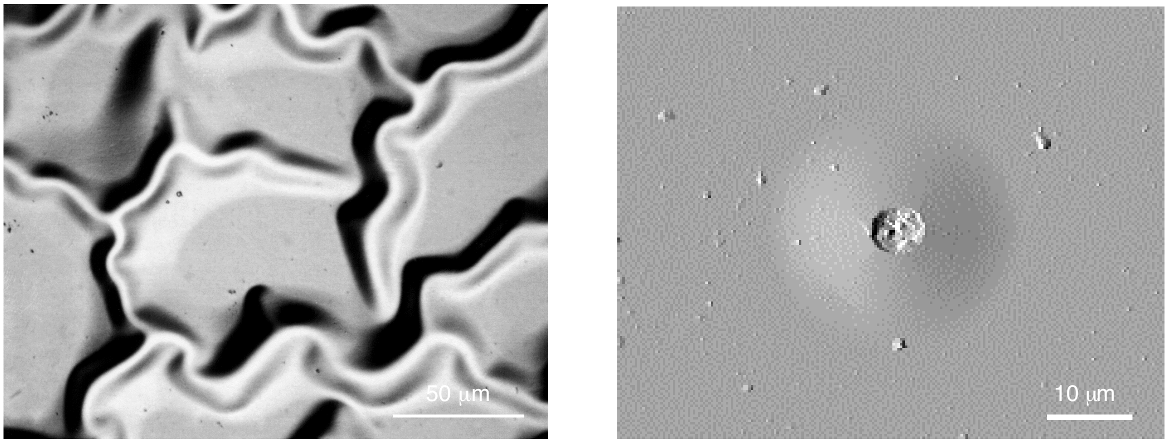
Fracture

Previous work [17] showed that deposition of the tantalum nitride overlayers triggered extensive delamination and telephone cord blistering on the as-deposited gold film sample and to a lesser extent over the as-deposited gold-on-chromium film sample. (Figure 3a) The blistered material readily spalled away exposing the lower fracture surface. High resolution SEM coupled with energy dispersive spectroscopy revealed that fracture had occurred along the film-sapphire interface. The freshly exposed sapphire surfaces under the telephone cord and the circular blisters were visually smooth at 50kX and showed no evidence of gold or chromium indicating that fracture occurred by interfacial decohesion. [18,19]



(a) (b) (c)

Figure 2. Composition profiles of the (a) as-deposited film, (b) the film annealed at 400˚C for 2 hours and (c) the film annealed at 400˚C for 8 hours show that diffusion during annealing has depleted the continuous chromium adhesive layer.



(a) (b)

Figure 3. Telephone cord blistering triggered by deposition of a stressed overlayer is shown for the (a) as-deposited gold film. A circular blister triggered by nanoindentation is shown for the (b) 400˚C/2h annealed gold-chromium film.

Nanoindentation was then used to induce interfacial fracture in the annealed films where telephone cord blistering did not occur. (Figure 3b) These tests triggered formation of large circular spalls. In all cases fracture occurred by reverse or double buckle formation during indentation with the material under the indenter pinned to the substrate [9]. The fractures in the partially annealed samples also occurred along the chromium-substrate interface. In contrast, all fractures in the long term annealed sample occurred along the tantalum nitride-gold interface. Moreover, the size of the blisters were smaller and the loads at fracture higher than observed in the partially annealed samples indicating that these samples were more resistant to interfacial fracture than any of the other samples tested.

Fracture Analysis

The uniform width and circular blisters provide the data from which interfacial fracture energies can be obtained using solutions for film systems where residual stresses dominate fracture behavior. These solutions were originally derived for single layer film-on-substrate systems [20-22]. Work by Bagchi et al. [11,12] and more recently by Kriese et al. [8] extended these solutions to multilayer systems by treating the multilayer film as a single film of the same total thickness with a transformed moment of inertia. The approach and results for the as-deposited films is presented in previous work.

Failure in the as-deposited gold and gold-chromium films occurred by telephone cord blistering. Under steady state conditions, the width of the telephone cord blister remains fixed creating a straight-sided blister with growth occurring along the more or less circular end of the blister. This gives a steady state fracture energy, Γ_{ss}, as follows [21],

$$\Gamma_{ss} = \left[\frac{(1-\bar{\upsilon}^2)h\sigma_r^2}{2\bar{E}}\right]\cdot\left(1-\frac{\sigma_b}{\sigma_r}\right)^2 \tag{1}$$

where h , E and ν are the multilayer film thickness, elastic modulus, and Poissons' ratios respectively, σ_b is the stress for delamination modified for multilayer films, and σ_r is the average residual stress.

Failure in the accelerated aged samples required nanoindentation to trigger delamination and circular blister formation. In all blisters, the center is constrained giving rise to a reverse or double buckle configuration. Following the analyses of Marshall and Evans [21] and Evans and Hutchinson [22], the strain energy release rate for formation of a circular blister at fracture due to residual and indentation stresses, $\Gamma(\psi)$, is given by

$$\Gamma(\psi) = \frac{(1-\bar{\upsilon}^2)h\sigma_v^2}{2\bar{E}} + (1-\alpha)\frac{(1-\bar{\upsilon}^2)h\sigma_r^2}{\bar{E}} - (1-\alpha)\frac{(1-\bar{\upsilon})h(\sigma_v-\sigma_c)^2}{\bar{E}} \tag{2}$$

TABLE I.

FRACTURE ENERGY RESULTS FOR AS-DEPOSITED GOLD AND GOLD-CHROMIUM FILMS.

Film	h_{Au} (nm)	h_{Ta_2N} (nm)	2b/2c (μm)	σ_b/σ_c (μm)	σ_r (GPa)	$\Gamma_{SS}/\Gamma(\psi)$ (J/m^2)	ψ	Γ_I (J/m^2)
Au								
As-deposited	200	275	28.8	0.3	-1.4	1.3	-75	0.5
Au-Cr								
As-deposited	200	450	57.8	0.1	-1.8	2.9	-82	0.9
400˚C/2h	200	490	29.9	0.5	-1.8	2.8	-67	1.3
400˚C/8h	200	490	15.4	5.6	-1.8	11.8	-68	5.3

where $\alpha=1-[1+0.902(1-\nu)]^{-1}$ [20], σ_c is the stress for delamination, and σ_v is the stress from indentation.

The uniform width and circular blister fracture energies are mixed mode values consisting of shear and normal contributions. The normal contribution is critical to understanding mechanisms controlling susceptibility to interfacial fracture. Of the criteria proposed to describe the relationship between mixed mode and mode I contributions, $\Gamma_I=\Gamma(\psi)/[1+\tan^2\{(1-\lambda)\psi\}]$ [20,23], is most often used. In this equation, λ is a material parameter equal to 0.3 for most materials, and ψ is the phase angle of loading.

Average blister widths and diameters, delamination stresses, residual stresses, mixed mode and mode I fracture energies, and phase angles of loading are given in Table I for the uniform width blisters in as-deposited gold and gold-chromium films and circular blisters in the annealed gold-chromium films. The as-deposited gold film fracture energy of 0.5 J/m^2 is in very good agreement with the true work of adhesion from contact angle measurements of gold on sapphire. [18] This is consistent with the observation that fracture occurred along the film substrate interface. The fracture energies for the gold-chromium films on sapphire are two times greater than for pure gold clearly demonstrating the better adhesion properties of chromium interlayers. Interestingly, the fracture energies increase slightly for samples where the chromium interlayer is reduced in size. Complete depletion of the chromium adhesive layer led to a marked increase in fracture energies. In addition, the fracture path changed from along the film-substrate interface to along the overlayer-gold film interface. Diffusion has replaced the thin hard chromium adhesive layer with a solid solution of gold and chromium in the lattice and enhanced concentrations of chromium along the gold grain boundaries. Gone also is the resistance to deformation that nanometer scale features possess. The solid solution of gold and chromium deforms much more readily than the chromium interlayer facilitating crack tip plasticity and dislocation emission. Moreover, it appears that crack nucleation has become much more difficult without the hard interlayer. It is unlikely that adhesion improved with the transition from a continuous chromium interlayer to a gold-chromium solid solution. There are no reactions between film and substrate at these temperatures or in samples held at high temperatures for much longer times. [24] As a result, the increase in fracture resistance following annealing appears attributable to the effects of interfacial structure on deformation and fracture while chromium in solution remains as effective an adhesion promoting agent as it is forming a continuous interlayer.

CONCLUSIONS

In this study, highly compressed overlayers were combined with nanoindentation to study the effects of diffusion during post deposition annealing on susceptibility to interfacial fracture of gold and gold-chromium films used in hybrid microcircuits. The gold films formed with 5-nm-thick twins along the substrate interface while the chromium interlayers formed a complementary structure along the substrate interface in the gold-chromium films. Highly stressed overlayers were combined with nanoindentation to induce delamination and blister formation from which fracture energies were determined. The results on as-deposited films showed that chromium increased the work of adhesion from 0.5 to 0.9 J/m^2. Tests on the annealed films showed that the films remained bonded at a similar strength level as long as the adhesive layer remained essentially continuous along the substrate. However when diffusion led to chromium layer depletion, fracture changed from the film-substrate interface to the overlayer-film interface accompanied by a three-fold increase in fracture energies. This change in fracture path and increase in fracture energies appears attributable to formation of a gold-chromium solid solution that promotes deformation while inhibiting interfacial fracture.

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REFERENCES

1. Mittal, K. L. (1976) *Electrocomponent Science and Technology*. 3, 21..
2. Mattox, D. M. (1973) *Thin Solid Films*. 18, 173.
3. Munitz, A. and Komem, Y. (1976) *Thin Solid Films*. 37, 171.
4. Thomas, R. E. and Haas, G. A. J. (1972) *Appl. Phys*. 43, 4900.
5. Rairden, J. R., Neugebaur, C. A. and Sigsbee, R. A. (1971) *Metall. Trans*. 2, 719.
6. George, M. A., Glaunsinger, ,W. S., Thundat, T. and Lindsay, S. M. (1990) *Thin Solid Films*, 189, 59.
7. Munitz A. and Komem, Y. (1980) *Thin Solid Films*, 71, 177.
8. Kriese, M. D., Gerberich, W. W. and Moody, N. R. (1999) *J. Mater. Res*. 14, 3007.
9. Moody, N. R., Hwang, R. Q., Venkataraman, S., Angelo, J. E., Norwood, D. P. and Gerberich, W. W. (1998) *Acta mater*. 46, 585.
10. Kriese, M. D., Moody, N. R. and Gerberich, W. W. (1998) *Acta mater*. 46, 6623.
11. Bagchi, A.and Evans, A. G. (1996) *Thin Solid Films*. 286, 203.
12. Bagchi, A., Lucas, G. E., Suo, Z. and Evans, A. G. (1994) *J. Mater. Res*. 9, 1734.
13. He, M. Y., Evans, A. G. and Hutchinson, J. W. (1996) *Acta metall. mater*. 44, 2963.
14. Moody, N. R., Medlin, D., Boehme, D. and Norwood, D. P. (1998) *Engng. Fract. Mech*. 61, 107.
15. Sun, R. C., Tisone, T. C. and Cruzan, P. D. (1975) *J. Appl. Phys*. 46, 112.
16. Cullity, B. D. (1956) *Elements of X-Ray Difffraction*. Addison-Wesley Publishing Co., Reading, MA.
17. Moody, N. R., Adams, D. P., Volinsky, A. A., Kriese, M. D. and Gerberich, W. W. (2000) In: *Interfacial Engineering for Optimized Properties II*, Briant, C., Carter, C., Hall, E., and Nutt, S. (Eds.)., Mater. Res. Soc. Proc. 494, pp. 195-205, Pittsburgh, PA.
18. Reimanis, I. E., Dalgleish, B. J., Brahy, M, Ruhle, M. and Evans, A. G. (1990) *Acta metall. mater*. 38, 2645.
19. Reimanis, I. E., Dalgleish, B. J. and Evans, A. G. (1991) *Acta metall. mater*. 39, 3133.
20. Hutchinson, J. W. and Suo, Z. (1992) In: Advances in Applied Mechanics. 29, pp. 63-191, Hutchinson, J. W. and Wu, T. Y. (Eds.) Academic Press Inc., New York.
21. Marshall, D. B. and Evans, A. G. (1984*) J. Appl. Phys*. 56, 2632.
22. Evans, A. G. and Hutchinson, J. W. (1984) *Int. J. Solids Struct*. 20, 455.
23. Thouless, M. D., Hutchinson, J. W., and Liniger, E. G. (1992) *Acta metall. mater*. 40, 2639
24. Zhao, X.-A., Kolawa, E. and Nicolet, M.-A. (1986) *J. Vac. Sci. Technol. A*. 4, 3139.