Studies on the Al_2O_3-Ti-Mo-Au metallization system*

J. M. Harris, E. Lugujjo,† S. U. Campisano,‡ and M.-A. Nicolet

California Institute of Technology, Pasadena, California 91125

R. Shima

Jet Propulsion Laboratory, Pasadena, California 91104

(Received 19 August 1974; final form 27 September 1974)

The behavior of Ti–Mo–Au metallization on Al_2O_3 and C has been investigated by backscattering spectrometry. Results show that Mo–Au bimetal films typically mix during deposition. Diffusion of Ti in Mo film occurs at 600°C, but is inhibited by the presence of oxygen in the Ti film. Even 1000 Å of Mo is not a barrier against interdiffusion of Ti and Au during 20-min anneals at 600°C. The amount of mixing observed also depends on the nature of the substrate which supports the Ti–Mo–Au metallization.

I. INTRODUCTION

With the ever-increasing duration of space flights, which is approaching ten years,[1] methods must be developed to determine the long-term reliability of electronic components. Many problems exist in achieving optimum reliability of integrated circuits. One of these problems involves multilayer metallization structures.[2] Industry has been plagued by poor substrate metallization adhesion and poor thermocompression bonds using both wire and beam leads.

To gain understanding of these failures, multilayer structures were prepared and analyzed by backscattering spectrometry.[3] This technique is particularly well suited to such an investigation, because it is fast, nondestructive, and is currently available to us courtesy of the Kellogg Radiation Laboratory at Caltech.

II. EXPERIMENTAL PROCEDURE

Metals were deposited on 1-μin.-finished Al_2O_3[4] and on polished C by electron-beam evaporation at pressures of less than 3×10^{-6} Torr and by rf sputtering using high-purity argon as the sputtering gas.[5] Anneals were performed in an evacuated quartz tube furnace at pressures of less than 8×10^{-5} Torr and temperatures ranging from 200 to 800°C.

Films were analyzed by $^4He^+$ backscattering spectrometry both before and after annealing. Backscattering is a convenient tool for thin-film analyses since it possesses both mass and depth perception. This allows one to determine both concentration profiles and film thicknesses. Mass perception arises through the energy loss incurred by that small fraction of the incident $^4He^+$ particles which are backscattered from the target nuclei. The energy, E'', of these particles after scattering is related to their energy, E', before scattering by

$$E''=K_ME', \quad (1)$$

where K_M is the factor for $^4He^+$ elastic backscattering by 168° from mass $M(K_{Au}=0.923,\ K_{Mo}=0.847,\ K_{Ti}=0.718)$.

$^4He^+$ particles also lose energy by interacting with electrons as they penetrate the target. This gives rise to a depth scale, which can be ascertained by simply knowing the particles' incident energy, the energy loss per unit path length (dE/dx), the elastic scattering factor (K_M), and the exit energy E. For targets which are only a few thousand Ångstroms thick, and at incident energies of the order of 2.0 MeV, the energy loss in both the incoming and outgoing paths is proportional to the path length. Thus, backscattering from atoms below the surface generates exit energies of

$$\begin{aligned}E&=K_ME_0-\Delta E\\&=E_1-[S]x,\end{aligned} \quad (2)$$

where E_0 is the incident beam energy, K_ME_0 is the energy of a particle backscattered from the surface, $[S]$ is the depth factor which depends on K_M and dE/dx, and x is the depth at which scattering occurred.

The area under the backscattering signal from a given element [see Fig. 1(a)] is proportional to the scattering cross section and to the number of atoms of that element which are subtended by the beam. The scattering cross section, σ, depends on the atomic number of the target material, Z_M, and the energy of the particle just before scattering, E', as

$$\sigma\propto(Z_m/E')^2. \quad (3)$$

Thus, concentration ratios are easily determined by taking the ratio of the cross-sectionally weighted areas under the signals of interest.

Concentration profiles are also easily determined since a variation in the atomic concentration of a given element with depth corresponds to a variation in the height of the backscattering signal with energy. However, the beam loses energy while penetrating the target; therefore the scattering cross section changes

 Copyright © 1975 by the American Vacuum Society

with depth. Thus, even a constant concentration will give nonconstant spectrum height and this may give an untrained eye the illusion of a concentration gradient. However, this is a small effect in thin films and incident energies around 2.0 MeV because the beam energy changes only slightly, even after completely traversing the film. The main features discussed above are illustrated in Fig. 1(a), which is an idealized backscattering spectrum of Mo–Au on C target. Carbon is a preferred substrate for thin-film analysis by backscattering because the signal from possible oxygen contamination in the film appears at energies higher than the carbon signal.

A typical beam area is 1 mm^2. The resulting spectrum is, therefore, an average of the backscattering signals over this area. The above discussion of backscattering assumes that a sample is laterally uniform over this area. This assumption must be checked for each sample.

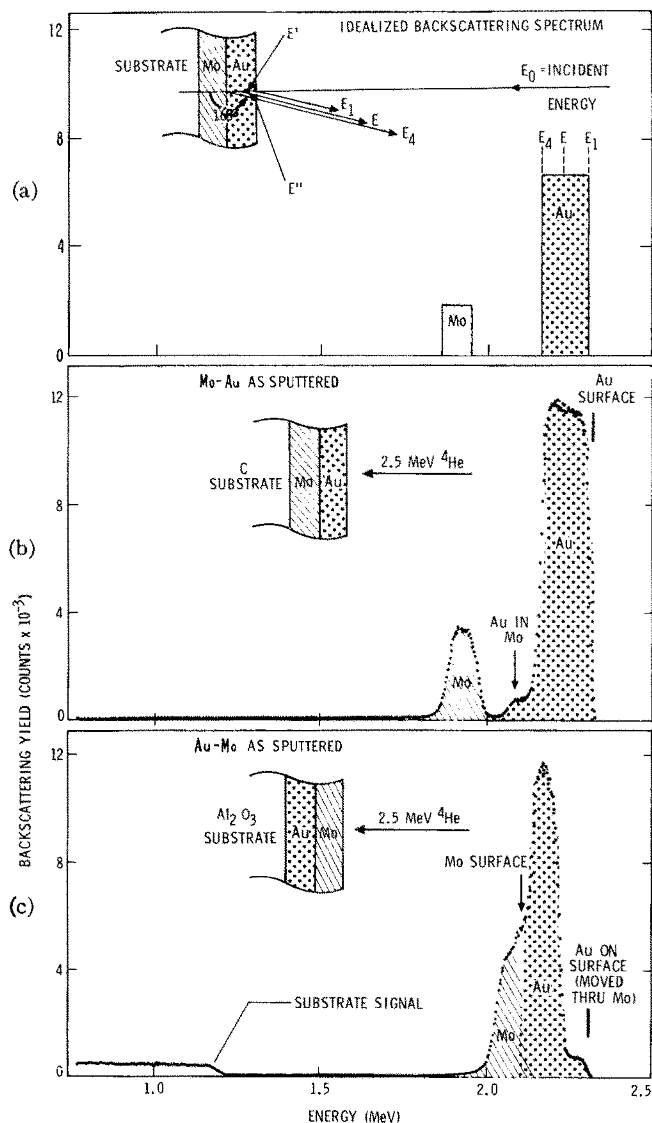

FIG. 1. (a) Schematic representation of spectrum due to backscattering on two superimposed thin films. The leading edge of the Mo peak is shifted below the energy corresponding to surface backscattering because of the energy loss experienced by particles in traversing the Au film. (b) Energy spectrum due to 2.5 MeV $^4He^+$ backscattering on an unannealed Mo–Au films couple. Thicknesses of Au and Mo films are 1100 and 800 Å, respectively. (c) Energy spectrum due to 2.5 MeV $^4He^+$ backscattering on an unannealed Au–Mo films couple. Thicknesses of Mo and Au are 680 and 700 Å, respectively.

III. RESULTS AND DISCUSSION

The behavior and analysis of trimetal layers can be complicated. We therefore first analyzed the bimetal couples of Mo–Au and Ti–Mo.

A. Mo–Au

Figure 1(b) shows a typical spectrum of 2.5-MeV $^4He^+$ backscattered from an as-desposited sample of a Mo layer sputtered on a carbon substrate with an overlaying sputtered gold film. The Au signal extends to energies lower than those corresponding to the Au–Mo interface. This result can be explained by assuming that a fraction of the deposited gold has moved into the Mo film. To verify this interpretation we prepared a sample with a reversed layer sequence on an Al_2O_3 substrate. The corresponding backscattering spectrum is shown in Fig. 1(c). Again we find the Au extending into the Mo film. Both results confirm the presence of some Au in the Mo film after sputtering. Furthermore, the choice of substrate does not show a significant effect.

According to the Au–Mo phase diagram the solid solubility of Mo in Au is of the order of 0.5–1 at.% in the temperature range between 200 and 800°C while the solid solubility of Au in Mo is exceedingly small.[6] We find 2–3 at.% of Au in Mo. This result cannot, therefore, be interpreted in terms of bulk properties. It has been shown for evaporated thin-metal films that small grain size is correlated with high melting point.[7] In a bimetal thin-film couple the small grain size in the film of higher melting point allows an easy penetration of the species with the lower melting point. The observed concentration of 2–3 at.% Au in Mo is typical of such grain-boundary diffusion in immiscible metals.[8] To test this assumption, we prepared a sample by evaporation of Au onto sputtered Mo. In contrast to sputtering, typical substrate temperatures during Au evaporation are less than 100°C. In this case mixing also occurred. Since diffusion coefficients for grain-boundary diffusion are typically high, it is reasonable that Au is present in Mo at these low temperatures.

B. Ti–Mo

Recent work with V has shown that oxygen plays an important role in determining the behavior of easily oxidized thin-metal films.[9] Since Ti has a strong affinity to oxygen, we expected oxygen to affect the behavior of Ti–Mo thin-film couples as well. To test this hypothesis we performed experiments on two different sets of samples. After Ti evaporation one set was oxidized while the other set was not. A Mo layer was then deposited on both sets. Figures 2(a) and (b) show the spectra of an unoxidized and oxidized sample after

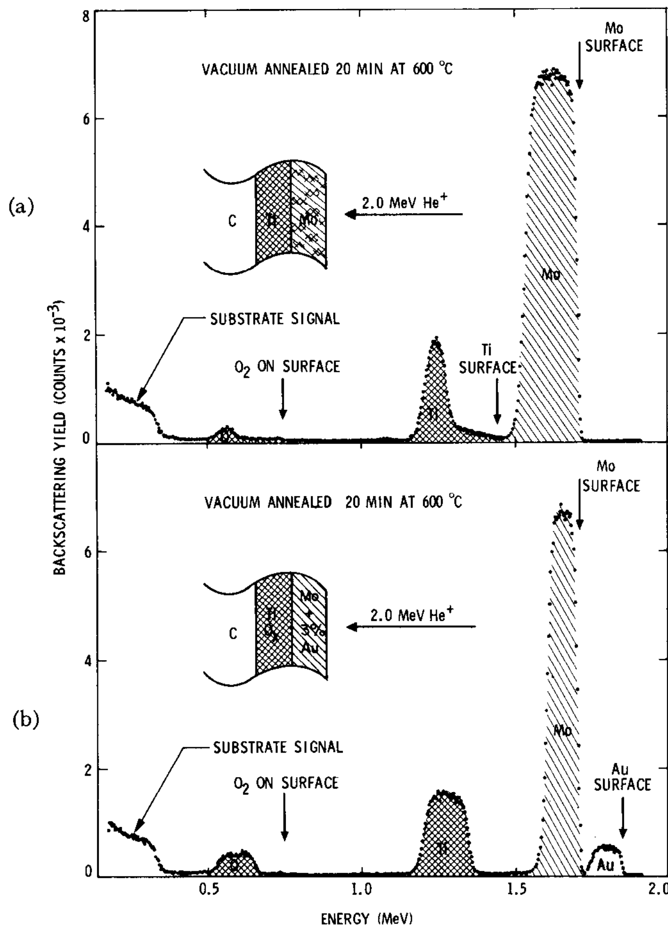

FIG. 2. (a) 2.0 MeV $^4He^+$ backscattering spectrum from 1400 Å of Mo covering 900 Å of Ti which have been vacuum-annealed for 20 min at 600°C. (b) Energy spectrum due to 2.0 MeV $^4He^+$ backscattering on an 800-Å Mo film covering a 1100-Å TiO_x film vacuum-annealed for 20 min at 600°C in an 8×10^{-6} Torr vacuum. From the ratio between areas of the Ti and O peaks, the value of x is 3.25. Also present is an accidental 3% Au contamination in the Mo.

simultaneous annealing in vacuum for 20 min at 600°C. The comparison indicates that Ti in the oxidized sample does not move, whereas Ti in the other sample does. (Some oxygen, though, was acquired by Ti in the unoxidized sample during annealing.) The different behavior of oxidized and unoxidized Ti with respect to diffusion in Mo is a clear indication of the importance of oxygen in determining diffusion processes of Ti.

At 600°C the phase diagram for the Ti–Mo system predicts a solid solubility of Mo in Ti of about 1 at.% and a wide range of solid solutions of Ti in Mo (from 0 to about 82 at.%).[6] The experimental result of Fig. 2(a) shows instead that after 20 min at 600°C Ti is present in Mo in concentration of roughly 3 at.%. This discrepancy with the phase diagram could be attributed to an inhibiting effect of the oxygen, in which case a truly oxygen-free Ti–Mo couple might behave quite differently.

C. Ti–Mo–Au

It follows from the preceding results that in an unannealed Ti–Mo–Au triple layer, Au permeates the Mo film at a level of several at.%, so that Au is in contact with Ti in spite of the Mo layer. Figure 3(a) shows that this is indeed the case for a sample obtained by sequential sputter depositions. A backscattering spectrum of the same sample after vacuum anneal at 600°C for 20 min is given in Fig. 3(b). This spectrum reveals that some 30% of the Au is now located below the Mo film, and that about 50% of the Ti is above the Mo film. Yet, the Mo film itself has changed little in thickness and appears to contain only small amounts of Au and Ti. The Ti motion seen here is much larger than that observed during a similar anneal without the presence of the Au film (see Fig. 2), although the final oxygen content is similar in both cases. The reason for this difference is unclear. It could be caused by direct interaction of Au with Ti or by an influence of the Au on the Ti–O interaction.

If one assumes that the motion of Ti and Au is diffusion-limited and follows the law $x^2=Dt$, a diffusion constant of the order of magnitude of 10^{-14} cm^2/sec is required to explain the transport observed. A value of this magnitude is consistent with the idea of grain-boundary diffusion.[10]

IV. EFFECTS OF SUBSTRATE

It has been shown in connection with Figs. 1(b) and (c) that the substrate does not affect the Au diffusion through Mo grain boundaries in unannealed samples. We repeated the 20-min anneal at 600°C with a Ti–Mo–Au triple layer sputtered on a 1-μin. finished

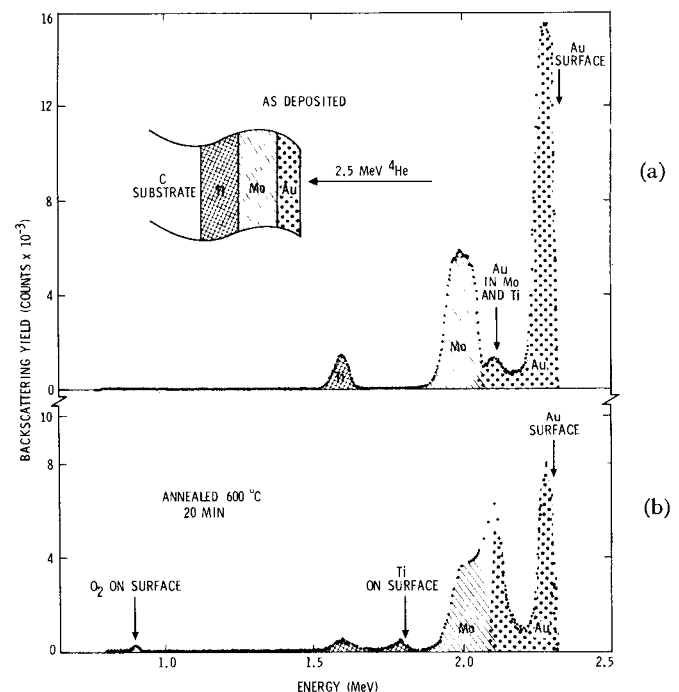

FIG. 3. (a). Energy spectrum due to 2.5 MeV $^4He^+$ backscattering from a 750-Å Ti, 1000-Å Mo, and 550-Å Au sputtered trilayer film on a carbon substrate. (b) Energy spectrum obtained in the same experimental conditions of Fig. 3(a) but after 20 min annealing at 600°C in an 8×10^{-6} Torr vacuum.

Al_2O_3 substrate. The result shows that in this case much more mixing occurs than on the carbon substrate. Substrate effects have been reported in the literature.[11] Further studies are in progress.

V. CONCLUSION

Mo–Au bilayers typically mix during deposition. Furthermore, 1000 Å of Mo is not a barrier to Ti–Au mixing at 600°C anneals for 20 min. Oxygen shows an inhibiting effect on the movement of Ti through Mo.

ACKNOWLEDGMENT

We would like to express our grateful appreciation to Motorola, Scottsdale, Arizona, for their participation in this project.

*Work supported in part by NASA (J. Maserjian and J. Boreham, JPL).

†Present address: Bell Telephone Research Labs, Murray Hill, N.J. 07074.

‡Permanent address: Istituto di Phisica, University of Catania, Italy.

[1] R. R. McDonald and W. S. Shipley, Astron. Aeron. **8**, 36 (1970).

[2] G. L. Schnable and R. S. Keen, IEEE Sixth Reliability Physics Symposium Proceedings p. 170 (1967).

[3] W. K. Chu, J. W. Mayer, M.-A. Nicolet, T. M. Buck, G. Amsel, and F. Eisen, Thin Solid Films **17**, 1 (1973).

[4] Alsimag 805 manufactured by American Lava Corp., Div. 3M, Laurens, SC 29360.

[5] R. Shima, J. Vac. Sci. Technol. **11**, 71 (1974).

[6] M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw–Hill, New York, 1958).

[7] J. P. Hirt and K. L. Moazed, Phys. Thin Films **4**, 60 (1969).

[8] S. U. Campisano, G. Foti, F. Grasso, and E. Rimini, J. Vac. Sci. Technol. **12**, 448 (1975).

[9] H. Kraütle, M.-A. Nicolet, and J. W. Mayer, J. Appl. Phys. **45**, 3304 (1974).

[10] C. Weaver, *Physics of Thin Films*, edited by M. Francombe and R. Hoffman (Academic, New York, 1971), Vol. 6, p. 315.

[11] W. Rhodes, R. C. Sunduhl, and L. Bernin, Natl. Bur. Std. Special Pub. **348**, 271 (1971); R. Sunduhl, J. Vac. Sci. Technol. **9**, 181 (1972).