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DIFFUSION AND STRUCTURAL CHANGES IN MICROCIRCUIT INTERCONNECTIONS

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Diffusion and Structural Changes in Microcircuit Interconnections

Welville B. Nowak

Abstract

The interdiffusion of platinum and gold films, a couple utilized in beam-lead microcircuits, has been studied for temperatures up to 550°C, Gold-on-platinum couples and separate platinum and gold films, 80-450 nm thick, were deposited by electron beam evaporation onto oxidized (111) silicon substrates. Diffusion was monitored by means of spectral reflectance versus wavelength in the band 500-1000 nm. The separate metal films showed good adhesion and stable reflectances (after an initial change) for at least 6 h at diffusion temperatures, in contrast to the couples. Analysis of platinum diffusion through the gold films yielded an activation energy about 38 kcal/g-atom and a pre-exponential factor of the order $10^{-3} cm^2/sec$, values close to those for volume diffusion. The pre-exponential factor expecially is dependent upon film deposition conditions.

The work presented here was a continuation of the research previously reported in the document "Final Report, NASA Research Grant NGR-22-011-007, Inter-relations Between Advanced Processing Techniques, Integrated Circuits, Materials Development and Analysis" dated 1 June 1971, by W.B. Nowak, B.L. Cochrun, W. Carlson, A. Grabel, of Northeastern University, Boston, Massachusetts.

Substantially the same techniques were used here as detailed in the above referenced report. Better defined and more accurate data were taken systematically. An analysis technique was developed that permitted an evaluation of both the activation energy for diffusion and the diffusion coefficient for the case of platinum diffusing through gold films.

The results of this work were presented in a paper delivered at the Fifth International Vacuum Congress, Boston, Massachusetts, October 13, 1971, and have also been published as the following paper: "Diffusion in Thin Film Couples of Platinum-Gold" by Welville B. Nowak and Richard N. Dyer, The Journal of Vacuum Science and Technology, Vol. 9, pages 279-283, 1972. A copy of this paper is attached.

Diffusion in Thin Film Couples of Platinum–Gold*

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The interdiffusion of platinum and gold films, a couple utilized in beam-lead microcircuits, has been studied for temperatures up to 550°C, Gold-on-platinum couples and separate platinum and gold films, 80–450 nm thick, were deposited by electron beam evaporation onto oxidized (111) silicon substrates. Diffusion was monitored by means of spectral reflectance versus wavelength in the band 500–1000 nm. The separate metal films showed good adhesion and stable reflectances (after an initial change) for at least 6 h at diffusion temperatures, in contrast to the couples. Analysis of platinum diffusion through the gold films yielded an activation energy about 38 kcal/g-atom and a pre-exponential factor of the order 10^{-3} cm^2/sec, values close to those for volume diffusion. The pre-exponential factor especially is dependent upon film deposition conditions.

Introduction

In recent years a demand has arisen for thin film metal systems that will perform reliably as microcircuit interconnections and that are compatible with the circuit fabrication processes. Aluminum is successfully and conveniently used in many cases. In other cases, aluminum film interconnections have failed because of interactions with gold, SiO_2, silicon, oxygen, or water vapor, or because of mass migration at high current densities. Consequently, multilayers of different metals have been investigated and utilized.[1–6] Failure mechanisms in multilayers include diffusion, chemical reaction, electromigration, and stress relief.

Reported here is an investigation of the interdiffusion of evaporated Au-on-Pt films, a combination used for "beam-lead" microcircuit connections.[6] Spectral reflectance over the visible band at the film surfaces provided an index of the concentration at (or near to) the surface.

Experimental Details

In our early experiments, the Au and Pt films were deposited on ordinary microscope slides or on Corning 7059 aluminoborosilicate glass microscope slides. The slides are advantageous in that both sides of the couple can be examined optically, but they have the disadvantage that film behavior (adhesion and solubility in substrate) differs from the practical situation. Therefore, the data reported here was obtained on oxidized Si wafer substrates. About 1 μm of SiO_2 was thermally grown on polished, (111) Si wafers, 2.54 cm in diameter, by oxidizing them for nine hours at 1000°C in wet oxygen.

Au and Pt films were deposited on three such wafers (labeled A, B, and C) simultaneously by electron beam evaporation of the respective metals from individual pyrolytic graphite crucibles. First the Pt and then the Au was evaporated in a single pumpdown cycle. Pressures were about 1×10^{-5} Torr in an oil-pumped vacuum system with liquid nitrogen cold traps. The Si wafer substrates were heated to 100°C for the Pt deposition and then were cooled to ambient temperature in about 10 min by thermal conduction to water-cooled posts. The Au was deposited at ambient temperature. During evaporation, the radiant heat raised substrate temperatures by 10°C. A shutter covered the substrates until the Pt or Au charges were molten and evaporating. Evaporation rates were about 1000 Å/min.

A stainless steel sliding mask, remotely moved between the Pt and Au depositions, defined three areas (approximately 2.0×0.7 cm) on each substrate. The center area was the Au-on-Pt couple, and the adjacent areas were Pt and Au single metal monitor films, respectively. The monitors were used for judging thickness, reflectance, and adhesion of the separate films.

Because of fixture geometry in the evaporator, the three substrates were tilted and displaced with respect to a perpendicular from the center of the crucibles. This resulted in source-substrate distances of 10, 11, and 12 cm, and in angles of incidence (with respect to substrate normals) of 8°, 22°, and 29° for wafer positions A, B, and C, respectively. Consequences of this geometry are (1) a film thickness variation from position A to C, and (2) a structural variation as evidenced in the diffusion results.

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For each deposition, the three substrates A, B, and C were simultaneously heat treated in air in a temperature controlled furnace (±5°C) for about 5 min at 450°, 475°, 500°, 525°, or 550°C. Spectral reflectance measurements were then taken at room temperature. This procedure was repeated for heat treatment intervals generally doubling the previous time, up to a total of about 6 h.

Spectral reflectance was measured at normal incidence by directing monochromatic light into a metallurgical microscope (with the film specimen on the stage) and detecting the light output of the eyepiece with a silicon solar cell. The solar cell was loaded with a 1000-Ω resistor, and the voltage across the resistor (5–500 μV) provided a measure of the reflected light. The combination of monochromator slit dimensions and microscope magnification resulted in a specimen effective area of 0.35×0.72 mm. This is large enough to average out small inhomogeneities in the film, yet small enough to allow various parts of a specimen to be sampled.

Absolute reflectivities were obtained using fresh MgO or "White Reflectance Paint" (Eastman Kodak Co., Rochester, N. Y., catalog No. 6086) as standards to correct for the spectral response of the optical system and detector. Agreement with literature values to within a few percent was obtained for various metal films over the range 500–1000 nm. For most measurements, however, it was more convenient to use an aluminum film as a secondary standard.

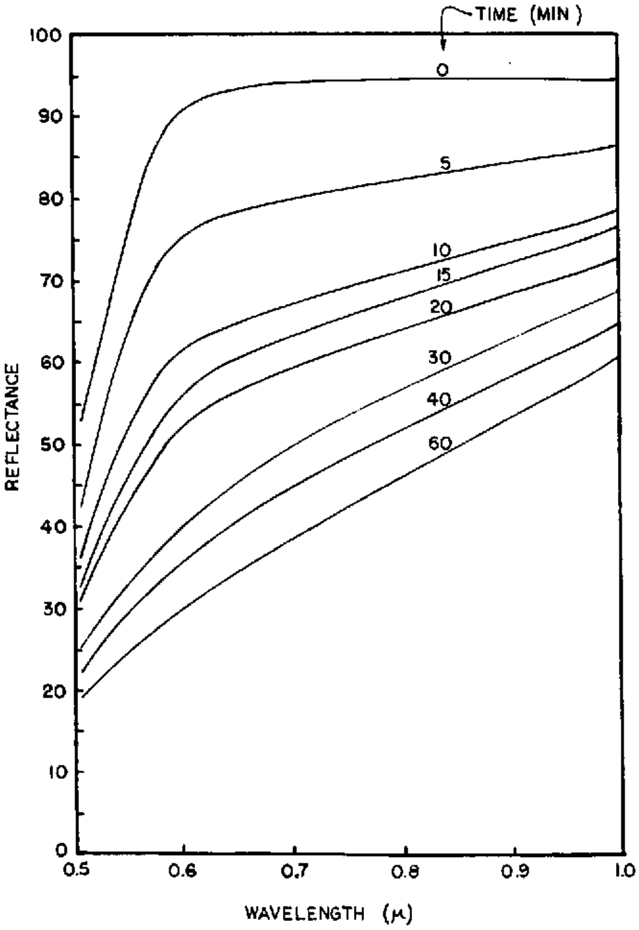

FIGURE 1. Normalized reflectance vs wavelength curves from the data of Fig. 1.

Results and Discussion

The Au monitor films remained stable in reflectance and resisted physical deterioration, such as loss of adhesion, throughout the experiments. The Pt monitor films, after an initial rapid change (to be reported elsewhere), also exhibited stable properties. The Au/Pt couples, however, often blistered, lost adhesion, and peeled off the substrate. When this happened, they always curled with the Au film inside, giving evidence of a tensile stress in the Au film. The Pt film may have a compressive stress, since there was a marked tendency for buckling or "crinkling" of the Pt films on the glass slides.

Electron microscope examination of 1000-Å films from specimens heat treated at 475°C for 10 h revealed an average grain size of about 10^4 Å in the gold films of both couple and monitor, with grains larger and smaller by a factor of 2. In some areas the Au grains had a substructure with cells about 10^3 Å on a side. Occasional pin holes appeared in the couple Au film, but not in the monitor, and the Pt film structure could be seen through the hole. The Pt structure appeared as small dark dots and ill-defined dark regions in a uniform light matrix. The average size of the dark portions was about 200 Å.

As a result of the heat treatments, the couple Au surface was somewhat silvery, similar to the appearance of Au–Pt alloys. Typical spectral reflectivity curves of a couple Au film after annealing in air for various times are shown in Fig. 1. For clarity, the data points are not shown in the figure; they were taken every 0.1 μm from 0.5 to 1.0 μm, inclusive, and are within ±1% of the curves except for a few stray points. Since only the curve shapes are taken as indicators of composition (thus removing extraneous factors that might uniformly affect the reflectance magnitude), each curve was normalized to its value at 1.0 μm. Figure 2 shows plots of a normalized reflectance vs wavelength for the curves of Fig. 1.

The slopes of the normalized curves between 0.6 and 1.0 μm show a fairly steady increase with time, which we interpret as indicating an increase in Pt concentration. An average measure of the slope at any time was taken as the sum of the change in normalized reflectance from time zero at $\lambda=0.6$ and 0.7 μm, i.e.,

$$\Sigma\Delta\mathrm{NR}=[\mathrm{NR}(0)-\mathrm{NR}(t)]_{0.6}+[\mathrm{NR}(0)-\mathrm{NR}(t)]_{0.7}.$$

Typical plots of ΣΔNR vs time are shown in Fig. 3. Each curve may be roughly divided into two regions: an extremely rapid increase followed by a very slow increase or plateau. A transition point between these regions was defined by the intersection of two straight lines approximating the curves in the two regions. The time at this transition point was chosen as an indicator of the diffusion rate. That is, when the character of the spectral reflectance changes abruptly it is assumed that a certain concentration of Pt is at the Au surface. The slight dip in the curves of Fig. 3 for the thicker specimens was a general occurrence. We are unsure of its origin.

Arrhenius plots were made by finding the natural logarithm of the ratio of gold film thickness squared to the time of the transition point and graphing this logarithm vs the reciprocal absolute temperature, as shown in Fig. 4. The value 32.2 in the ordinate scale of Fig. 4 is related to the conversion of $(\text{Å})^2/\text{hr}$ to cm^2/sec. Data relating to Fig. 4 are presented in Table I. The data at 500°C have been omitted because they lay significantly above the lines for unknown reasons. For a diffusion coefficient expressed by $D = D_0 \exp(-Q/RT)$, values of the activation energy Q calculated from Fig. 4 are 39, 38, and 34 kcal/g-atom for the A, B, and C series, respectively. These values are probably accurate to ±5%. Since the activation energy for volume diffusion of Pt into Au is 39 kcal/g-atom,[7] we conclude that Pt is moving through the Au film predominantly by volume diffusion.

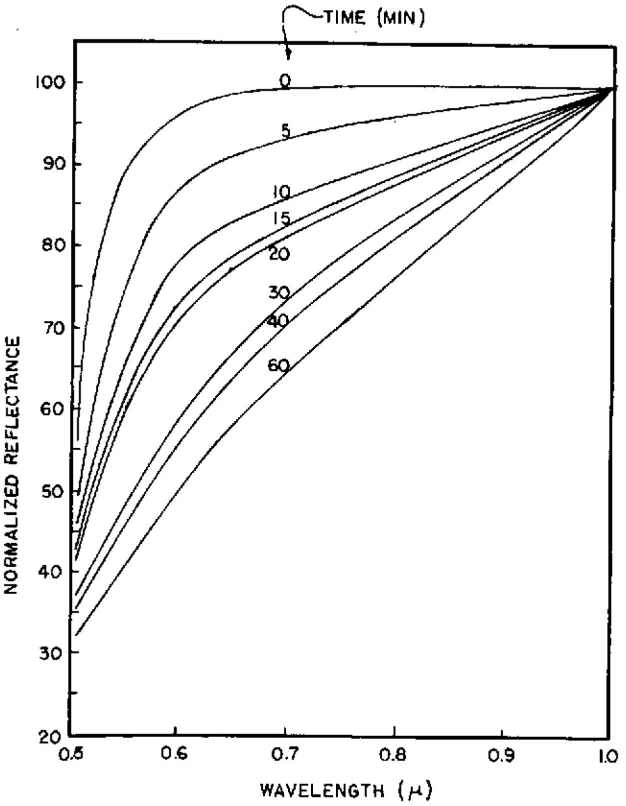

FIGURE 2. Typical reflectance vs wavelength curves for progressive times of diffusion at a fixed temperature. Specimen 56A.

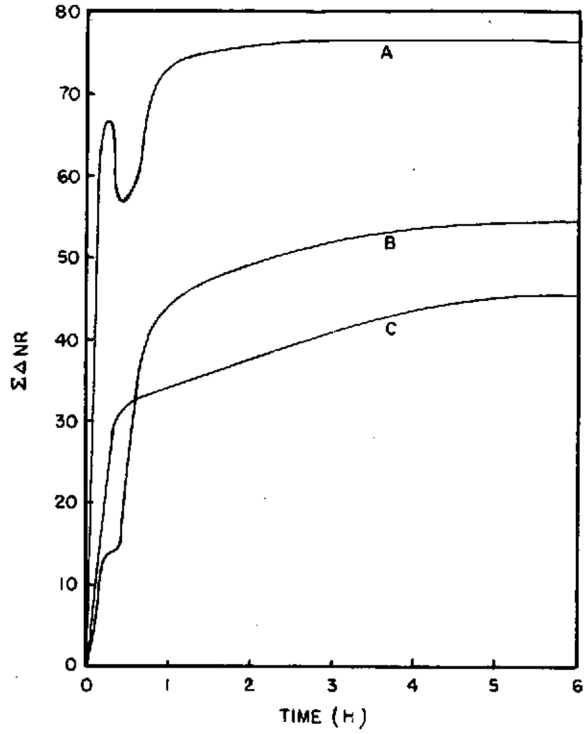

FIGURE 3. Changes in the slope of the normalized reflectance curves at large wavelength vs diffusion time. Specimen 58.

To find whether the value of D_0 also corresponds to volume diffusion the Pt concentration at the Au surface must be known. Attempts to produce calibrating alloy films by electron beam and flash evaporation from bulk alloys were unsuccessful. Instead, the Pt concentration was estimated by matching experimental data to theory.

The Au–Pt phase diagram has a large, solid-state miscibility gap, extending from 15 to 98 at.% Pt in Au at about 500°C.[8] In such a case, the concentration profile contains an interface at which the Pt concen-

TABLE I. Data used for Arrhenius plots shown in Fig. 4.

Specimen	Film thickness (Å) Pt	Film thickness (Å) Au	Diffusion temperature (°C)	Transition time (h)
55A	2730	2160	450	4.0
55B	1920	1210	450	2.0
55C	1270	780	450	1.6
57A	4450	3000	475	4.0
57B	2730	2300	475	2.25
57C	1000	1150	475	1.0
58A	4000	2730	525	1.0
58B	2730	2400	525	0.60
58C	1300	770	525	0.21
56A	...	3000	550	0.47
56B	...	2500	550	0.40
56C	...	1000	550	0.15

tration drops from 0.98 to 0.15 discontinuously.[9] For our diffusion conditions and with reasonable values for the diffusion coefficients of Pt in Au and Au in Pt,[10] one may calculate that the interface motion is very small. Thus, the Pt concentration is effectively held at 0.15 at the original Pt/Au interface.

The concentration C of the Pt at the free surface of a Au film of thickness L is given by

$$\frac{C}{C_0}=1+\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{2n+1}\exp\left[-\frac{Dt(2n+1)^2\pi^2}{4L^2}\right],$$

where $C_0=0.15$ at the other boundary. Solutions of this equation were compared with experimental transition times and thicknesses, and consistent matching was found for $C/C_0 \simeq 0.9$, i.e., near the solubility limit. This would also correspond to the level at which the change of $\Sigma\Delta NR$ with concentration becomes small if the reflectivity of Au–Pt alloys were similar to that of Au–Pd.[11] Table II presents the values of D obtained by the above matching. Values of D_0, also given in Table II, were calculated from D and the appropriate Q value. It should be noted that $D_0=1.2\times10^{-3}$ cm²/sec for volume diffusion.[7] Therefore, we may again conclude that volume diffusion predominates, but is somewhat modified by film structure. This is not too surprising since the surface area presented to the incident light for grains is 10^3 times that for grain boundaries in our films, and we would not expect to observe the direct effect of the grain boundaries, which would be quickly saturated to the solubility limit. It can be seen from Table II that reasonable agreement exists for D_0 and Q among films deposited at the same position (A, B, or C). This correlation appears much more consistent than one based upon film thickness, and is probably related to film structure. However, D is approximately proportional to thickness.

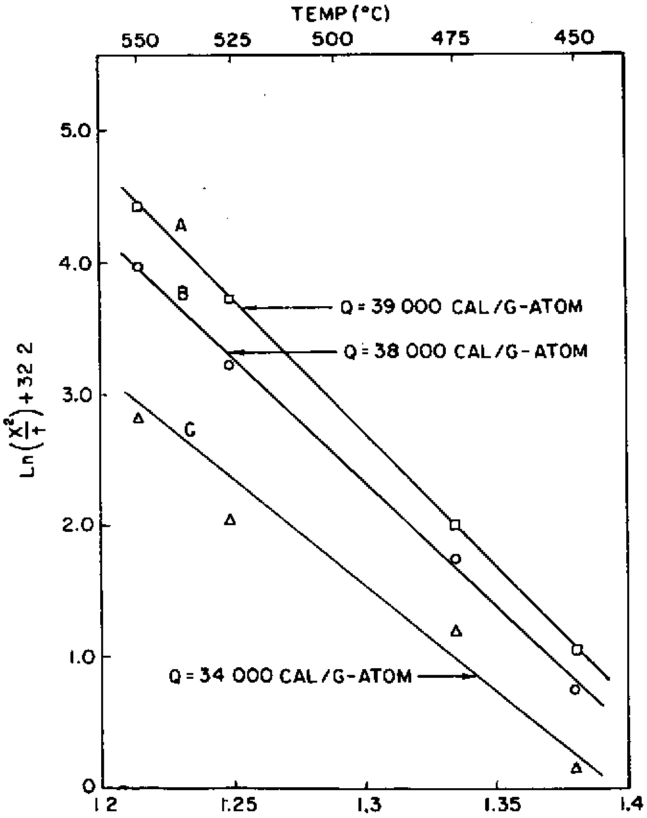

FIGURE 4. Arrhenius plots for the diffusion of Pt into Au in thin film couples on oxidized Si substrates.

TABLE II. Diffusion coefficient constants of Pt into Au for various film specimens.

Specimen	Au thickness (Å)	D (cm²/sec) $\times10^{14}$	D_0 (cm²/sec) $\times10^3$	Q (kcal/g-atom)
55A	2200	3.9	22	39
57A	3000	7.0	15	39
58A	2700	24	10	39
56A	3000	62	12	39
55B	1200	2.3	6.4	38
57B	2300	7.6	8.1	38
58B	2400	30	6.6	38
56B	2500	51	5.7	38
55C	780	1.2	0.19	34
57C	1150	4.3	0.32	34
58C	770	9.0	0.17	34
56C	1000	22	0.20	34

It is interesting to note that most of the metal film diffusion studies employing optical reflectivity,[12–15] including this study, led to the conclusion that volume diffusion predominated. One optical investigation, however, resulted in diffusion coefficients many orders of magnitude higher than the extrapolated volume coefficients.[16] Other investigators using electrical resistivity, x-rays, and electron microprobe techniques reported observations corresponding to grain boundary diffusion;[17,18] however, it should be noted that the grain sizes in those studies were 10–100 times smaller than in the work reported here. An intermediate case appears to be that of Rairden *et al.*[19]

Acknowledgments

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