JOURNAL OF MATERIALS SCIENCE 14 (1979) 873–881

The effect of temperature and humidity on interdiffusion of gold and titanium in thin films

W.D. SYLWESTROWICZ, H.A. ELKHOLY
Fairleigh Dickinson University, Madison, New Jersey, USA

G.W. KAMMLOTT
Bell Laboratories, Murray Hill, New Jersey, USA

Gold–titanium thin films are frequently used in a number of devices where gold is the conductor and titanium the bonding agent between gold and glass or ceramic substrates. Exposed to the corrosive environments, gold–titanium metallizations deteriorate and lead to failure of the devices. In this work, a preliminary study, the effect of humidity and temperature on interdiffusion of gold and titanium films was investigated. It was found that during the initial exposure period of gold–titanium thin film samples, the electrical resistance decreased. This decrease of electrical resistance occurs at temperatures as low as 70° C and can probably be ascribed to annealing processes in the samples. Exposure of the samples to higher temperatures results in the diffusion of titanium along the grain boundaries of the gold to the surface of the sample and in an increase of electrical resistance. It was observed that at 325° C titanium diffuses from grain boundaries into the gold grains and forms a gold–titanium alloy. An addition of the water vapour to the agron atmosphere does not noticeably affect the diffusion process. Optical microscope observations, of the titanium diffusion to the sample surface were confirmed by scanning electron microscopy and by X-ray fluoroscence counts in a scanning electron microscope.

1. Introduction

Gold–titanium thin films are frequently used in a number of devices in which gold is the conductor and titanium the bonding agent between gold and glass or ceramic substrates. Exposed to corrosive environments, gold–titanium metallizations deteriorate and lead to failure of the devices. In this work, the effects of humidity and temperature on gold–titanium thin films were investigated. It is well established that humidity in the presence of such corrosive agents as chlorine, ammonia, etc., is an important factor influencing the vapour-phase corrosive processes. However, it is not clear if humidity in the absence of those agents also affects gold–titanium metallization and, in particular, the interdiffusion process.

Devices containing gold–titanium metallization are used at quite high ambient temperatures (up to 200° C) and it is of considerable interest to know to what extent exposure to these temperatures can affect the reliability of these devices. It should also be kept in mind that since the cross-sections of the conductors in the printed circuit devices are of the order of 10^{-6} cm^2, even with very small currents, the density of the current is quite high. This might results in a significant increase in temperature of the conductors.

In recent years, a few papers have been published on the subject of interdiffusion in thin films, including papers on Au–Ti metallization.

A comprehensive survey of solid-phase reactions was recently published by Mayer *et al.* [1]. They were not concerned with any particular system of metallization but rather with general aspects of solid-phase reactions. It was pointed out that data obtained from the bulk samples cannot be used with thin film samples. They also suggested that grain-boundary diffusion may dominate the kinetics in thin films. The interdiffusion in Ti–Au–Pd systems on sapphire substrate was studied by Poate *et al.* [2]. They used the Rutherford back-scattering technique and obtained profiles of the average interdiffusion in Ti–Au, Ti–Pd, and Ti–Pd–Au systems. In their investigations, they concentrated on the effectiveness of palladium as a barrier preventing interdiffusion of titanium into the gold layer. Experiments were conducted in air and vacuum. In these authors' opinion, "In all probability Ti is undergoing grain-boundary diffusion through Au". Christou *et al.* [3] investigated Ta–Pt–Ta–Au and W–Au and refractory element combinations on silicon substrates. In addition to the Rutherford back-scattering technique used by Poate *et al.*, scanning electron microscopy, Auger electron spectroscopy and X-ray diffractometry were used with annealing temperatures between 350 and 550° C. The effectiveness of Ta–Pt–Ti and Ti–Pt combinations as barriers to gold–silicon interdiffusion was evaluated.

In all of the described investigations above only the average concentration of elements (such as Au, Ti, . . .) was evaluated at the preselected depth of investigated film. They did not differentiate between concentration at the grain boundaries and the interior of the grain and did not give enough information to establish the mechanism of diffusion. Moreover, tests, discussed in the above papers, were performed at temperatures at which formation of titanium oxides takes place, thus drastically changing the characteristics of thin films. The resistance of titanium oxides is orders of magnitude larger than that of titanium, and titanium oxides are semiconductors with a negative coefficient of thermal resistance.

Annealing of gold layers and interdiffusion of titanium onto the gold layers occurs only above specific temperatures. It should be expected that in the temperature range 300 and 500° C, these processes would occur in the investigated samples. When samples were exposed to lower temperatures (i.e. 75° C), it was not obvious that both of these processes occurred. Conclusions obtained from tests at higher temperatures are not always, therefore, applicable to the tests at lower temperatures.

It should be emphasized that under real life conditions of devices with thin film metallizations, temperatures are usually below 200° C and, therefore, below the temperatures of formation of titanium oxides. The interdiffusion between gold and titanium in thin films is, therefore, the main process affecting their properties.

It is a frequently practiced procedure to predict the behaviour of a device in prolonged applications on the basis of investigating its behaviour at higher temperatures. This procedure raises a number of questions, such as to what extent high temperature is equivalent to prolonged exposure at lower temperature for some chemical reactions, intermetallic diffusion and annealing. It was expected that the experiments discussed in this work would answer some of these questions.

TABLE I Experimental data for gold–titanium specimens

Experiment series	Specimen no.	Exposure			Water vapour (Torr)	R_0	R_r	R_T	$\frac{R_r - R_0}{R_0}$	$\frac{R_T - R_r}{R_0}$
		Temp (° C)	Days	Argon						
First	2	220	21	Wet	30	10.9	12.3	20.1	0.13	0.72
	6	85	21	Wet	30	10.9	10.1	12.4	−0.07	0.21
	4	25	21	Wet	30	10.7	10.4	10.8	−0.03	0.04
Second	2	240	35	Dry	–	11.3	16.0	26.8	0.42	0.96
	3	35	35	Dry	–	11.3	11.0	11.7	−0.03	0.06
	5	30	35	Room atmos.	–	12.2	11.0	11.6	−0.02	0.05
	1	325	35	Dry	–	–	–	–	–	–

TABLE II Determination of titanium diffusion through gold layer by scanning microscope X-ray fluorescent radiation

Exposure temp (° C)	Area	X-ray counts				
		$Au(M_{\alpha+\beta})$	$Ti(K\alpha)$	$(Ti)_c - (Ti)_e$	Centre $(Ti)_{325} - (Ti)_{240}$	Edge $(Ti)_{325} - (Ti)_{240}$
240	Edge	93 357	5 650	1321	9222	5350
	Centre	93 587	6 971			
325	Edge	83 645	11 000	5193		
	Centre	81 381	16 193			

2. Experiments

Experiments were conducted for the conditions shown in Tables I and II. Notations used in this paper are:

R_0 Electrical resistance of a sample at room temperature before the test

R_r Electrical resistance of a sample at room temperature after the test

R_t Electrical resistance of a sample at test temperature T after t time of exposure.

R_T Electrical resistance of a sample at test temperature T at the end of the test

Specimens were prepared in the following way. On the glass substrate the layers of titanium (99.97% purity) and gold were deposited by electron beam gun technique. The deposition of the gold layer on the titanium layer was performed in the same setting without breaking the vacuum of the system. The pressure after deposition was about 10^{-6} Torr. The appropriate shape of the sample was then obtained by the photoresist technique, etching the gold layer with a diluted solution of potassium iodide, and the titanium with diluted hydrofluoric acid.

The samples used in these experiments were gold–titanium samples (Fig. 1) formed by a gold layer deposited on a titanium layer. The samples were 3.05 cm long and 1.5×10^{-2} cm wide. The titanium thickness was about 750 Å, the gold thickness about 5000 Å. The film thicknesses were measured by the stylus-step method with the use of a Talysurf instrument made by Taylor Hobson. Sodium-free (barium, aluminium, silicates) Corning 7059 glass was used as a substrate.

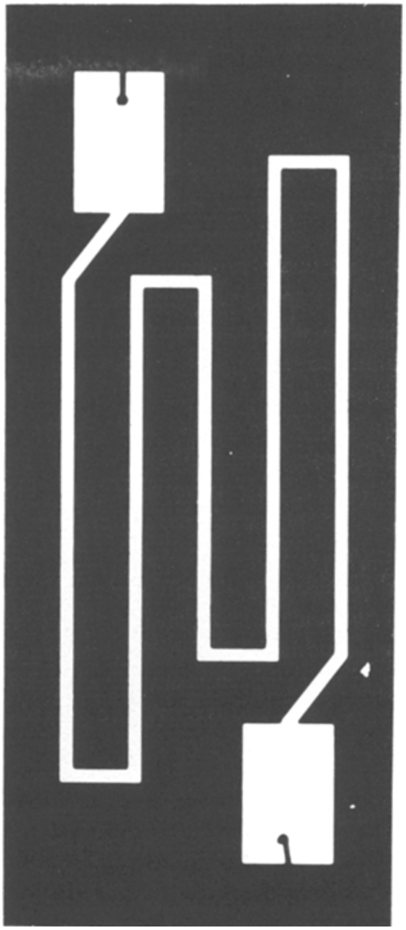

Figure 1 The shape of a gold–titanium sample is shown.

In this paper results obtained on the gold–titanium samples will be discussed. Six chips (samples on the glass substrate) were tested in six separate furnaces at different temperatures. These furnaces were inserted into a chamber which was also maintained at a constant temperature. This

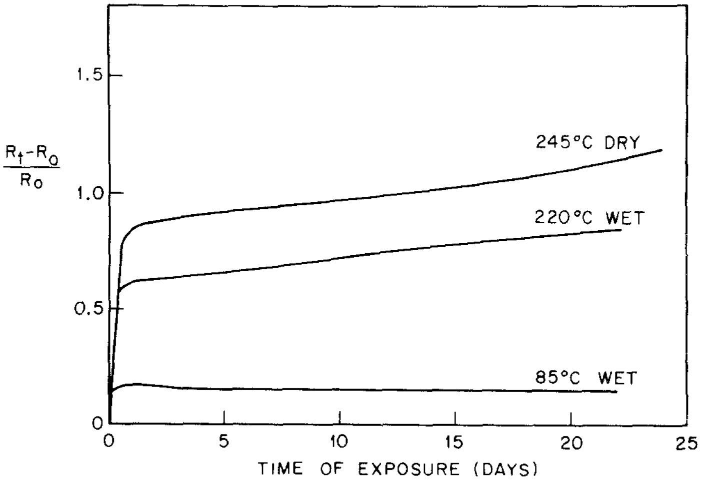

Figure 2 The increase of resistance with time of exposure is shown for three samples. Two samples were exposed at 85 and 220° C, respectively, to a wet argon atmosphere and the third was exposed at 240° C to a dry argon atmosphere.

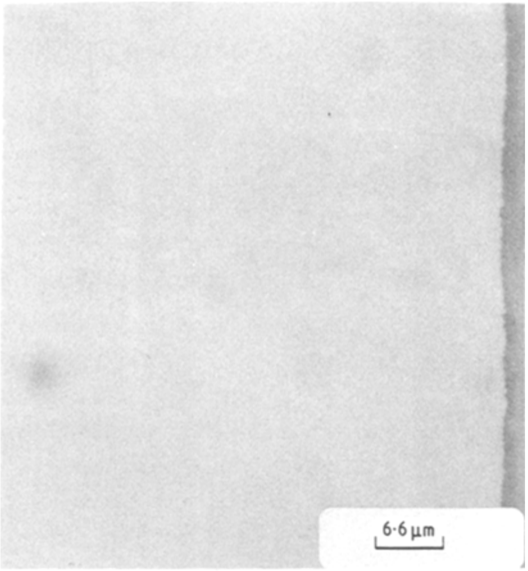

Figure 3 A microphotograph of the surface of a gold–titanium sample before exposure of the sample to a higher temperature.

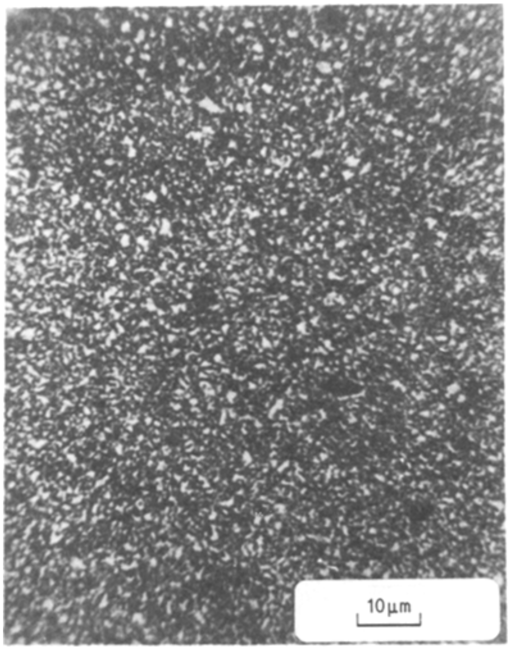

Figure 4 A microphotograph of the surface of a gold–titanium sample after 35 days exposure to the dry argon atmosphere at 240° C. A considerable amount of diffused titanium is visible around the gold grains.

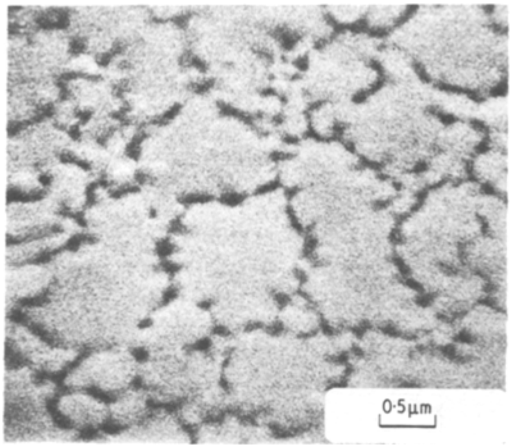

Figure 5 A microphotograph of the surface of a gold–titanium sample after 35 days of exposure to the dry argon atmosphere at 240° C. Grain boundaries are clearly delineated.

arrangement helped to maintain constant temperature in the furnaces during tests of long duration. In addition, in tests with a humid atmosphere, argon was fed to the furnaces through a gas-bubbling apparatus and pipings, all located in the chamber. The gas-bubbling apparatus was filled with deionized water. The water vapour pressure was regulated by the temperature in the chamber.

Samples were tested in the temperature range 25 to 325° C. Before heating the specimens, air from the entire testing system was pumped out and the system was flushed with argon for 18 h. During the tests, dry or wet argon was fed from a common source to the furnaces. The argon used was of 99.9999% purity. Samples were tested in two series of experiments for the conditions shown in Table I. The resistance of the samples was continuously recorded by drawing a current of 0.01 mA through the samples and measuring the voltage drop. In addition, the resistance of samples was periodically recorded directly. Before and after the experiments, the samples were examined under an optical microscope.

X-ray fluorescence counts, taken in a scanning electron microscope, with 20 kV accelerating voltage and 200 sec counting time, are shown in Table II. The X-ray counts are taken from two samples from the borders and central areas. The samples were exposed one to 240° C, and the second to 325° C. Before exposure of the samples, X-ray counts did not show any trace of titanium on the surface of the gold layer.

3. Experimental results

3.1. Gold–titanium specimens

Experimental data for gold–titanium specimens given in Table I and Fig. 2. At lower temperatures

(Table I, Fig. 2), after reaching a value corresponding to the test temperature, the electrical resistance decreased during the first several days of exposure, then remained constant. At higher temperatures the resistance increased continuously. Humidity did not noticeably affect the observed increase of resistance. By comparing the surfaces of the specimen before and after exposure at 240° C (Figs. 3 to 5), the diffusion of titanium along the grain boundaries could be seen clearly. Before exposure, the grain boundaries were indistinguishable on the surface of the samples (Fig. 3). In samples exposed to higher temperature, titanium diffused along the grain boundaries of the gold layer and delineated them (Figs. 4 and 5). When carefully examined at high magnification (Fig. 5), it seemed that diffusion occurred at discrete points at the grain boundary, and then from these points the titanium spread along the grain boundaries. At a higher temperature (325° C) titanium diffused from the grain-boundaries into the interior of the grains and probably formed one of the Au–Ti alloys (Figs. 6 and 7). Coagulations of titanium were also visible. In areas along the edges of the specimens, the diffusion of Ti was slower than in the middle of the specimen (Figs. 8 and 9). During formation of the samples by photo-resist technique, the etching agents penetrated to some depth into the sample at the interface of the gold and titanium layers, leaving corrosion products between the layers. These corrosion products represent a stronger diffusion barrier for titanium than the gold–titanium interface. In Fig. 10, at the edge of the gold layer grain boundaries are not clearly visible. Beyond this border area, diffusion is more advanced and the shape of the grain is clearly delineated. In samples exposed at 325° C diffusion was more advanced (Figs. 6 and 7) than in the samples exposed at 240° C (Figs. 4 and 5), and in the border area of the gold layer, grain boundaries could be seen (Fig. 9), but in the middle of the sample, the shape of grains was not clearly distinguishable. These visual observations were confirmed by elemental X-ray analysis (Table II). X-ray counts of titanium were larger in the middle of the sample than at the edge of the sample; 6971 against 5650 at 240° C and 16 193 against 11 000 at 325° C. Additional confirmation of the titanium diffusion through the gold layer at the grain boundaries was given by the SEM and X-ray analysis. The instrument used was a Cambridge Stereoscan IIA equipped with a Kevex X-ray detector and a Tracor multichannel analyser.

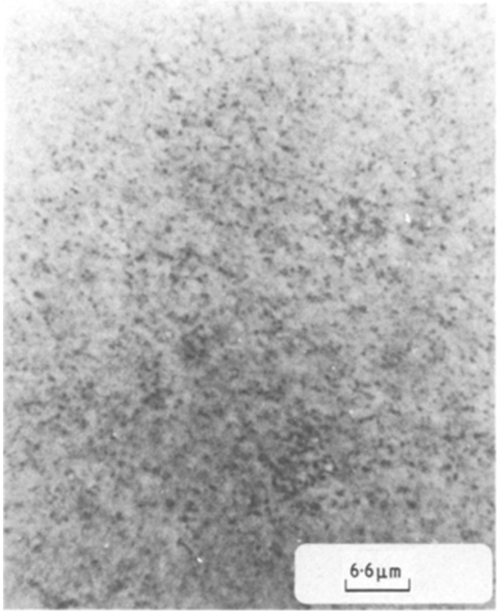

Figure 6 A microphotograph of the surface of a gold–titanium sample after 35 days exposure to the dry argon atmosphere at 325° C. No distinct separation is visible between the gold grains and the diffused titanium at the grain boundaries. Coagulations of titanium are visible.

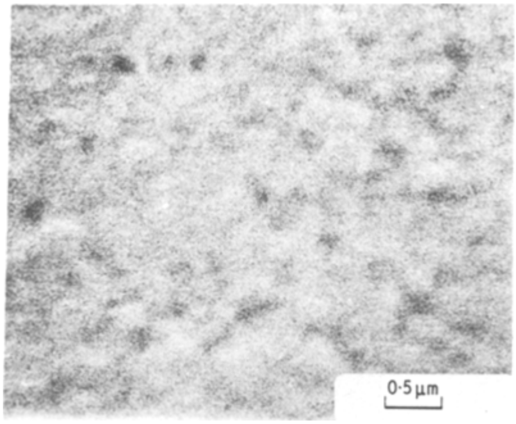

Figure 7 A microphotograph of the surface of a gold–titanium sample after 35 days exposure to the dry argon atmosphere at 325° C. No distinct separation is visible between the gold grains and the diffused titanium at the grain boundaries. Coagulations of titanium are visible.

The micrographs were taken in the backscatter mode, i.e. only the higher-energy portion of the secondary emission was used for imaging (Fig. 11a).

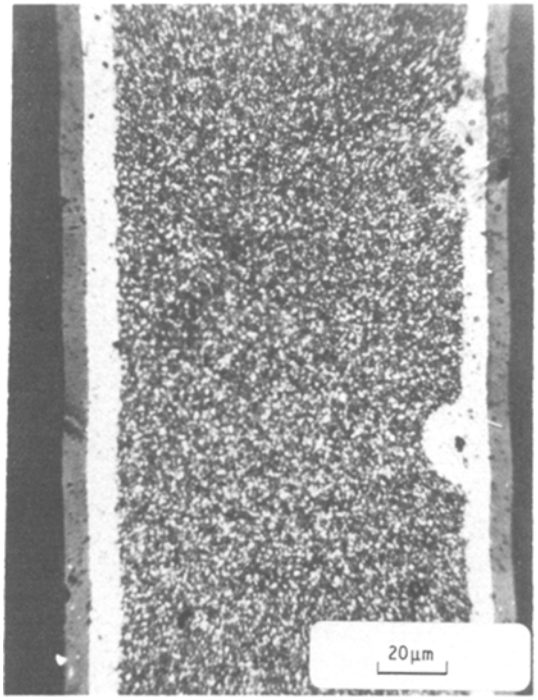

Figure 8 A microphotograph of the surface of a gold–titanium sample after 35 days exposure to the dry argon atmosphere at 240° C. A restricted diffusion of titanium at the edge of the sample gold layer can be observed. In the middle of the gold layer a considerable diffusion of titanium at the grain boundaries is visible.

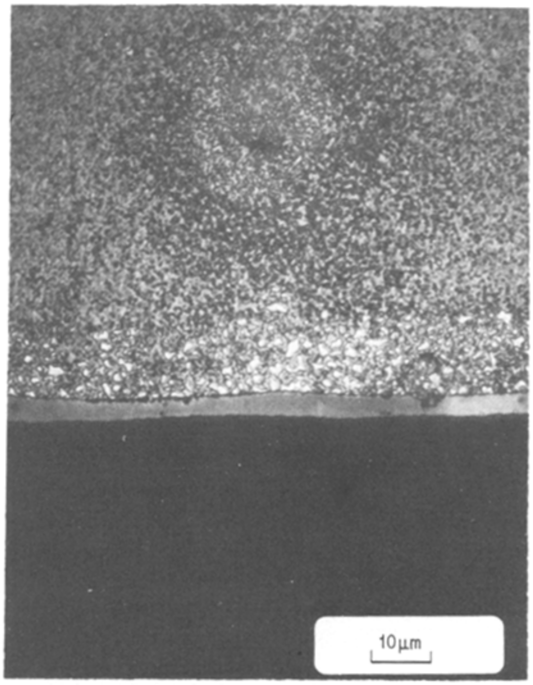

Figure 9 A microphotograph of the surface of a gold–titanium sample after 35 days exposure to the dry argon atmosphere at 325° C. The border area, undercut by the chemical agent during formation of the sample, and centre area with undamaged interface are shown.

Elemental X-ray analysis was obtained in two modes, either as spectrum or as elemental scan. To obtain a spectrum, a small area ($<= 1\,\mu m^2$) of interest was selected on the sample and scanned with the electron beam. The X-rays generated by the elements present within that small area were collected and displayed as a spectrum with the abscissa as energy and the ordinate as X-ray intensity. Comparison of peak heights of the gold and titanium obtained from within a grain and a grain boundary give information about their relative concentrations. Fig. 11c shows clearly that at the centre of the grain the titanium energy peak was not observed (line A). Measurements taken at the grain boundary show a distinct peak corresponding to the titanium concentration (line B).

To obtain somewhat more direct information, the elemental scan was used. In this mode the electron beam scans a single line dissecting one or more grains, respectively grain boundaries.

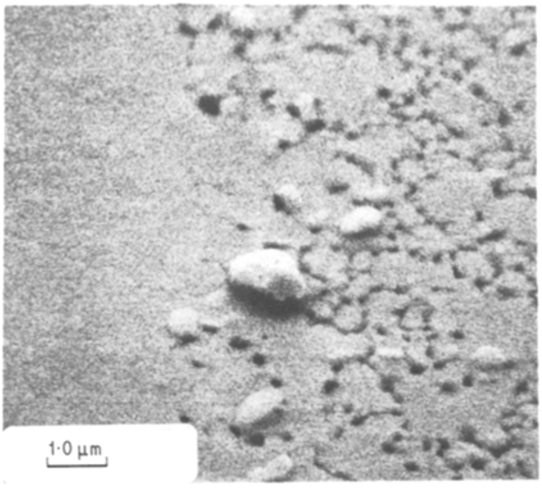

Figure 10 A microphotograph of a gold–titanium sample is shown. The specimen was exposed to the dry argon atmosphere for 35 days at 240° C. In the border area of the specimen a separation between gold grains and diffused titanium is not defined while in the centre it is clearly defined.

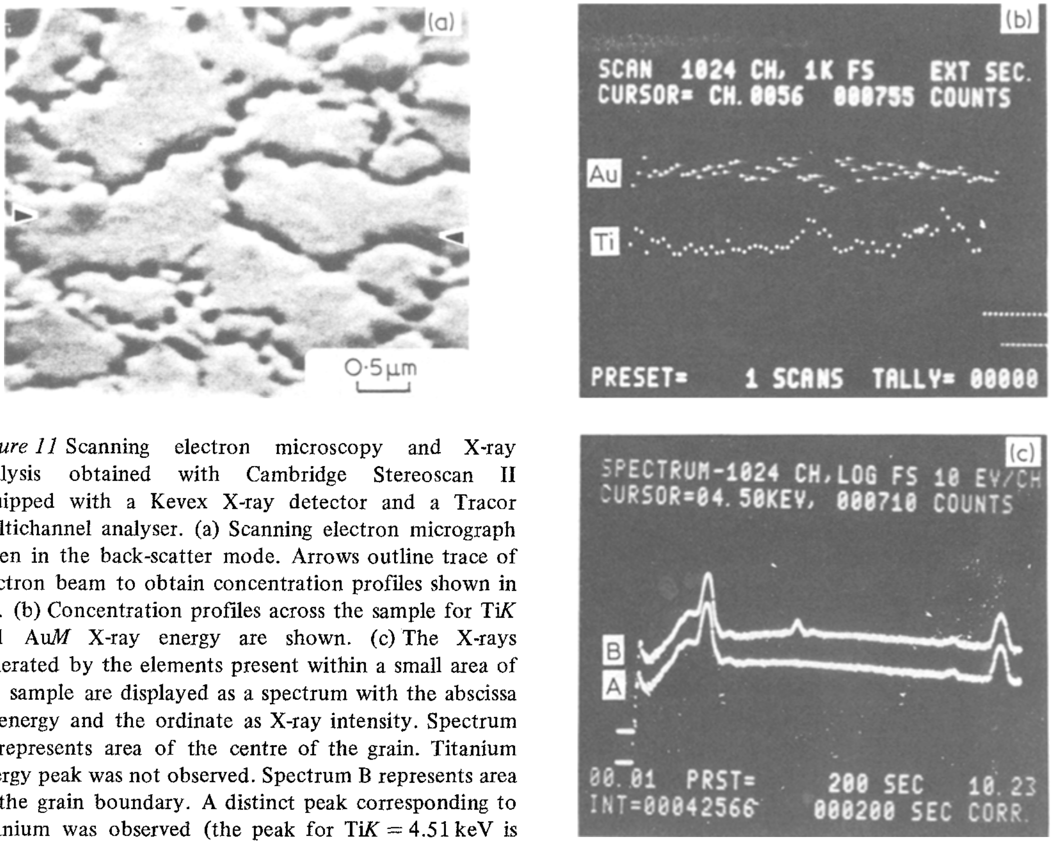

Figure 11 Scanning electron microscopy and X-ray analysis obtained with Cambridge Stereoscan II equipped with a Kevex X-ray detector and a Tracor multichannel analyser. (a) Scanning electron micrograph taken in the back-scatter mode. Arrows outline trace of electron beam to obtain concentration profiles shown in (b). (b) Concentration profiles across the sample for Ti*K* and Au*M* X-ray energy are shown. (c) The X-rays generated by the elements present within a small area of the sample are displayed as a spectrum with the abscissa as energy and the ordinate as X-ray intensity. Spectrum A represents area of the centre of the grain. Titanium energy peak was not observed. Spectrum B represents area at the grain boundary. A distinct peak corresponding to titanium was observed (the peak for Ti*K* = 4.51 keV is located almost in the centre of the spectrum).

The energy window of the multichannel analyser was set to collect either TiK or AuMK X-ray and their intensities were collected in consecutive channels. Thus an elemental concentration profile across the sample is obtained. Based on the information previously obtained by elemental X-ray analysis, the elemental concentration profiles showed an increase in titanium and a decrease in gold counts each time the electron beam crossed a grain boundary as shown in Fig. 11b. Occasionally this was not sharply defined, since the X-rays are collected from an approximately sphere-shaped volume with diameter of 1 to 2 μm and the grain boundaries did not necessarily meet the sample surface at right angles.

These experimental results finally confirmed that titanium was present in large concentrations at the grain boundaries of the sample exposed for 35 days at 240° C to the argon atmosphere. Diffused titanium is represented as dark areas on the grain boundaries.

4. Discussion

The experiments described in this paper were performed at temperatures below 250° C with one exception; a test at 325° C to observe the trend of changes. At a temperature of 325° C, not only was diffusion very strong and gold titanium alloys formed, but formation of titanium oxides was also expected [4]. In these experiments any reference to the sample resistance means the cumulative resistance of lattice inside the grains, grain boundaries, gold–titanium alloys, and titanium oxides. The range of temperatures from 75 to 250° C covers the temperatures to be expected under normal operating conditions of the components in printed circuits and is below the temperature of formation of titanium oxides, which drastically changes the characteristics of the films. By using an optical microscope with magnifications up to × 1200 and a scanning electron microscope with magnifications up to × 20 000, direct observations of the changes at the grain boundaries were made.

It can be assumed, with only negligible error, that in gold–titanium specimens the path of the electrical current is confined to the gold layer. In these samples electrical resistance is affected by lattice imperfections (dislocations, point defects), preferred orientation of the grains, and the amount and distribution of impurities present in the gold layer. Temperature, in addition to the change of the thermal coefficient of resistance and annealing processes, affects specimen resistance by accelerating the diffusion of titanium into gold.

During the initial period of exposure, a decrease of electrical resistance was observed. This can be seen more clearly at lower temperatures (Fig. 2), and is expressed by the parameter $\delta R_r = R_r - R_0$, when $\delta R_r < 0$ (Table I, Fig. 12). Probably this is due to the annealing of lattice imperfections. At higher temperatures, the decrease of resistance due to the annealing is obscured by the increase of resistance caused by diffusion. The rate of annealing also depends on the temperature and the time of annealing. There is a difference of opinion between the authors about the form of the time dependence of annealing. The diffusion of titanium into the gold layer results in an increase of resistance. Microscopic observations indicate that initially, as can be seen by comparing specimen surfaces before and after exposure, most diffusion occurs along the grain boundaries (Figs. 3 to 5 and 11). It is suggested here that the formation of a network of titanium film at the grain boundaries is responsible for the observed increase of electrical resistance in the gold–titanium specimens. In this model, electrical current must penetrate through the thin layers of titanium at each boundary, and the total specimen resistance consists of the sum of resistances of titanium thin films at the grain boundaries in a series with the sum of resistances of gold inside each grain. At a higher temperature (325° C), titanium from the grain boundaries diffuses into the grain (Fig. 6). The boundaries between individual grains disappeared. Coagulations of titanium are visible and the total amount of titanium on the surface increased (see Table II).

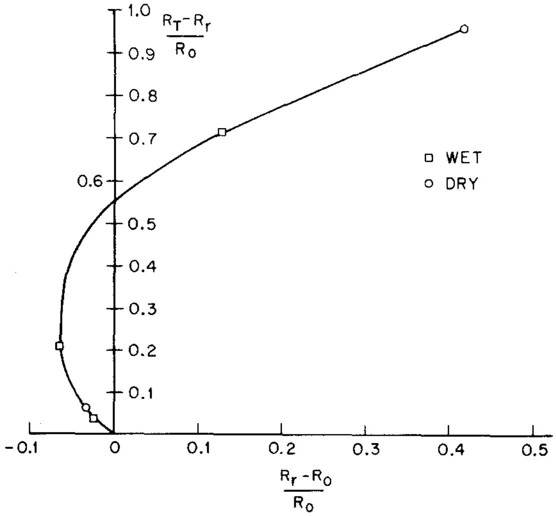

Figure 12 The relation between $(R_T - R_r)$ and $(R_r - R_0)$ is shown. Where $(R_T - R_r)$ is the difference at the end of the test between resistance at the test temperature and at room temperature and $(R_r - R_0)$ is the difference of resistance at room temperature after and before the test. The increases are normalized to the initial resistance R_0.

The nature of the alloys formed inside the grain was not determined, but variations in their stoichiometry should be expected: with the richer-in-gold alloy at the specimen surface and the richer-in-titanium close to the substrate. Humidity in the argon atmosphere does not noticeably affect changes in electrical resistance of the gold–titanium specimens (Fig. 2).

It is interesting to notice that the change of resistance before and after the test $(R_r - R_0)$, measured at room temperature, seems to characterize dependence of material resistance on temperature $(R_T - R_r)$ independently of the test conditions (Table I, Fig. 12). At lower temperatures the effect of annealing is predominant and the values of $(R_r - R_0)$ decrease.

It should be noted that the undercutting of the gold layer by etching does not result in the formation of a crack at the interface, but this area is filled with corrosion products. These corrosion products represent a stronger barrier for the diffusion than the gold–titanium interface: nevertheless, the diffusion of titanium does occur through the undercut area, and the titanium penetrates to the surface of the gold layer at the border area (Fig. 9, Table II).

Since the diffusion of titanium occurs mainly through grain boundaries and is not uniform across the cross-section of the specimens, the concept of a sharply defined interface in annealed specimens, where diffusion has occurred, is not realistic.

The effect of time of exposure is shown in Fig. 2. In this work, it was not attempted to determine the coefficient of diffusion of titanium into gold, to separate diffusion through grain boundaries or dislocations from diffusion through the bulk of gold inside the grain. To do so one would have to know the shape of grains not only in the plane of the surface, but their size in depth, the number of dislocations and their distribution, the diffusion coefficient for grain boundaries and dislocations, and the effects of point imperfections. Also, oxidation should be considered even at comparatively low temperatures. Taking all this into consideration, it seems to the authors that in this work any attempt to evaluate these factors would be an exercise in imagination.

5. Conclusions

During the initial exposure period of gold–titanium thin film specimens, a decrease of electrical resistance was observed. It is proposed here that this decrease of resistance is a result of the annealing processes in the samples and occurs at temperatures as low as 70° C.

Exposure of the specimens to a higher temperature results in the diffusion of titanium through the grain boundaries of the gold layer to the surface of the specimen, and an increase in electrical resistance. It was observed that at 325° C, after diffusion through the grain boundaries, titanium diffuses into the gold grains and forms gold–titanium alloys and distinct coagulations of titanium. An addition of water vapour to the argon atmosphere does not noticeably affect the diffusion process.

With the increasing temperature and time of the test, the interface between the titanium and gold layers becomes gradually less defined as the result of interdiffusion, and finally disappears altogether. An alloy of different stoichiometry, instead of two distinct layers, is probably formed.

Observations, by an optical microscope and scanning electron microscope, of the titanium diffusion to the specimen surface were confirmed by the X-ray fluorescence counts in a scanning electron microscope.

Acknowledgements

The authors would like to thank C. J. Doherty for preparing samples used, and P. A. Turner for his discussion of this work. The experimental part of this study was performed at Bell Laboratories, Murray Hill, New Jersey, while one of the authors (W.D.S.) was associated with them.

References

1. J. W. MAYER, J. M. POATE and KING-NING TU, *Science* **190** (1975) 228.
2. J. M. POATE, P. A. TURNER, W. J. DE BONTE and J. YAHALOM, *J. Appl. Phys.* **46** (1975) 4275.
3. A. CHRISTOU, L. JARVIS, W. H. WEISENBERGER and J. K. HIRVONEN, *J. Electron. Mater.* **4** (1975) 329.
4. W. D. SYLWESTROWICZ, *J. Electrochem. Soc.* **122** (1975) 1504.

Received 30 August 1977 and accepted 20 July 1978.