JOURNAL OF MATERIALS SCIENCE 15 (1980) 42–52

Effect of chlorine on gold–titanium thin films

W. D. SYLWESTROWICZ, H. A. ELKHOLY
Fairleigh Dickinson University, Madison, New Jersey 07940, USA

In this study the effect of a small concentration of chlorine on gold–titanium metallization was investigated. Samples were prepared by deposition of gold and titanium layers on a glass substrate. Samples were exposed at 75, 135 and 175° C for 53 days to an argon atmosphere and to an argon atmosphere containing 50 ppm chlorine. In all cases the electrical resistance of the exposed samples decreased and the addition of chlorine made this decrease even larger. Depending on the conditions, migration of the titanium atoms and formation of preferred oriented structure took place. At 135 and 175° C in the argon atmosphere containing 50 ppm chlorine, a very active migration of titanium atoms from the gold layer to the external surface of the samples was observed. Migration of titanium was not observed in the samples exposed to the pure argon atmosphere. This strongly suggests that chlorine acts as an agent bringing titanium from the gold layer to the external surface by a process known as chemisorption-induced segregation; on the surface titanium forms an oxide. When samples were exposed for 53 days at 175° C, preferred oriented structure in the gold layer was developed. Formation of the preferred oriented structure was neither conditioned nor related to the presence of chlorine in the atmosphere.

1. Introduction

The effect of environment on thin-film metallizations is of critical importance for a number of devices. Since the thickness of integrated circuits may be of the order of a few hundred atomic layers, environmental effects, which might be negligible in bulk materials, can be critical for these circuits. When the effect of environment is discussed, it refers to the effect of impurities; such as Cl_2, HCl, SO_2, NO_2, etc., present in the atmosphere. Data obtained for bulk materials are not always applicable to thin-film metallizations. Moreover, data obtained from one specific metallization or environment is not necessarily applicable to another metallization or environment. Even a very small concentration of impurities, a few part per million, can bring a catastrophic deterioration of a device [1].

It was believed that a concentration of a few ppm of chlorine in the atmosphere is detrimental to gold–titanium metallizations, but actually no data are available in the literature on the effect of chlorine on this particular metallization.

Preliminary to this study, an investigation on interdiffusion in gold–titanium metallization was conducted [2]. It was observed that in samples exposed at 85° C to the argon atmosphere, the resistance of samples decreased. With increasing temperature, the resistance started to increase and diffusion of titanium through grain boundaries to the external surface took place. Those observations are confirmed by the present investigations.

In this study, the effect of chlorine on the gold–titanium metallization was investigated. A comparison was made between samples exposed to the pure argon atmosphere and samples exposed to the argon atmosphere containing 50 ppm chlorine.

2. Experimental results

Samples were exposed at temperatures of 75, 135 and 175° C for 53 days to an argon atmosphere and to an argon atmosphere containing 50 ppm chlorine. During this exposure, the resistance of the samples was continuously monitored. Samples were examined before and after exposure by scanning Auger microprobe, under an optical microscope and X-ray diffrac-

0022–2461/80/010042–11$03.10/0

TABLE I Resistance of samples (Ω), measured before exposure (R_I), after 27 days exposure (R_{F_1}) and after 53 days exposure (R_{F_2}).

Atmosphere	Temperature (°C)	R_I	R_{F_1}	R_{F_2}	$R_{F_1}-R_I$	$R_{F_2}-R_I$	$R_{F_2}-R_{F_1}$	δ_1 (%)	δ_2 (%)
Argon	75	8.4	8.2	8.2	−0.2	−0.2	0		
		8.5	8.3	8.3	−0.2	−0.2	0		
		9.0	8.9	8.8	−0.1	−0.2	−0.1		
	Mean	8.63	8.47	8.43	−0.166	−0.2	−0.033	−1.85	−2.32
	Test of significance				signif. ($p = 0.05$)	signif.*	not signif. ($p = 0.40$)		
Argon + 50 ppm Cl_2	75	8.8	8.6	8.5	−0.2	−0.3	−0.1		
		8.7	8.4	8.4	−0.3	−0.3	0		
		8.6	8.4	8.3	−0.2	−0.3	−0.1		
	Mean	8.70	8.47	8.40	−0.233	−0.3	−0.066	−2.64	−3.45
	Test of significance				signif. ($p = 0.025$)	signif.*	not signif. ($p = 0.20$)		
Argon	135	9.4	9.1	9.0	−0.3	−0.4	−0.1		
		8.9	8.7	8.7	−0.2	−0.2	0		
		9.6	9.4	9.6	−0.2	0	0.2		
	Mean	9.30	9.07	9.10	−0.233	−0.2	0.033	−2.47	−2.20
	Test of significance				signif. ($p = 0.025$)	not signif. ($p = 0.40$)	not signif. ($p = 0.50$)		
Argon + 50 ppm Cl_2	135	8.9	8.6	8.6	−0.3	−0.3	0		
		8.3	8.0	8.0	−0.3	−0.3	0		
		8.4	8.1	8.2	−0.3	−0.2	0.1		
	Mean	8.53	8.23	8.27	−0.3	−0.266	0.033	−3.52	−3.05
	Test of significance				signif.*	signif. ($p = 0.025$)	not signif. ($p > 0.50$)		
Argon	175	8.8	8.7	8.7	−0.1	−0.1	0		
		8.6	8.5	8.5	−0.1	−0.1	0		
		8.6	8.5	8.5	−0.1	−0.1	0		
	Mean	8.66	8.57	8.57	−0.1	−0.1	0	−4.11	−3.65
	Test of significance				signif.*	signif.*	not signif. (no change)		
Argon + 50 ppm Cl_2	175	9.4	9.1	9.2	−0.3	−0.2	−0.1		
		8.8	8.4	8.5	−0.4	−0.3	−0.1		
		8.8	8.4	8.6	−0.4	−0.2	−0.2		
	Mean	9.00	8.63	8.76	−0.366	−0.233	−0.133		
	Test of significance				signif. ($p = 0.01$)	signif. ($p = 0.025$)	not signif. ($p = 0.10$)		

Effects of exposure where $\delta_1 = \dfrac{\text{mean } R_{F_1} - \text{mean } R_I}{\text{mean } R_I}$ $\delta_2 = \dfrac{\text{mean } R_{F_2} - \text{mean } R_I}{\text{mean } R_I}$

* No probability levels are given when all differences are the same and standard errors of difference equal zero.

tion photographs were taken. Experimental results are given in Tables I, II and III.

Samples were prepared by depositing layers of titanium (99.97% purity) and gold on a glass substrate through a mask using electron beam technique. The deposition of the gold layer on titanium was performed without breaking the vacuum system. The pressure after deposition was about 10^{-6} Torr. Three samples on the glass substrate form a chip, shown in Fig. 1.

Samples (Fig. 1) were of 3.3 cm length and 0.02 cm width. The titanium thickness was about 750 Å, the gold thickness about 5000 Å. The sample's thickness was measured by the stylus-step method with the use of a Talysurf instrument. Sodium-free (barium, aluminium, silicate) Corning 7059 glass was used as a substrate.

Six chips were tested in six furnaces. These furnaces were inserted into a chamber which was maintained at a constant temperature of 30° C.

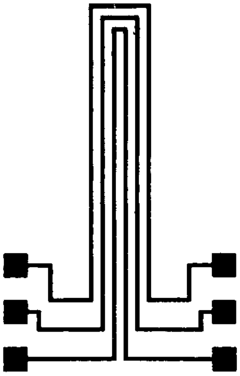

Figure 1 A chip formed by three samples located on a common glass substructure.

This arrangement helped to maintain a constant temperature in the furnaces during tests of long duration. Before heating the samples, air from the entire testing system was pumped out and the system was flushed with argon for 24 h.

During the test, argon was fed from a common source to the furnaces. The argon used was of 99.999% purity with traces of oxygen. Three chips were tested in argon atmosphere at 75, 135 and 175° C, respectively. Simultaneously, the remaining three chips were tested in the argon atmosphere containing 50 ppm of chlorine gas, also at 75, 135 and 175° C, respectively. It should be mentioned that all chips were made during the same evaporation. 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 at the room temperature was periodically measured (with higher accuracy) directly in the furnaces and recorded (see below).

2.1. Measurements of the resistance changes in the exposed samples

Changes of the resistance, recorded during the duration of the tests, were used only to observe the trend of the changes. The resistances of the samples were accurately measured at the room temperature at the beginning of the test, after 27 days of exposure and after 53 days of exposure and the values are given in Table I. The mean values of three samples located on the same chip also are given in this table and are used in the following computations. The initial resistance of the samples was about 9 Ω and was measured with an accuracy of 0.05 Ω.

It should also be mentioned that after 27 days exposure, when the temperature was reduced to room temperature and the resistance of the samples were measured, the whole system of furnaces remained closed and argon was continuously flowing through the system.

2.1.1. Experiments with samples exposed to the pure argon atmosphere

In samples exposed to the pure argon atmosphere, the samples' resistances depended on the temperature (Table I). The mean values of resistance at 75° C decreased with time of exposure from − 1.85% after 27 days of exposure to − 2.32% after 53 days of exposure. At 135° C the trend was reversed, from − 2.47% after 27 days of exposure to − 2.20% after 53 days of exposure, and remained constant at 175° C with − 1.04% after 27 and 53 days of exposure.

The statistical significance of changes was evaluated by the paired t-tests [3]. The changes of resistance after 27 days exposure were significant for all temperatures of exposure. For 75 and 135° C the value of p was 0.05 (probability 5%). For the samples exposed at 175° C, the standard error of difference was equal to zero, therefore the mean difference is obviously significant.

There were no statistically significant changes of the samples' mean resistance between the 27th and 53rd day of exposure.

2.1.2. Experiments with samples exposed to the argon atmosphere containing 50 ppm chlorine gas

In the samples exposed to the argon atmosphere containing 50 ppm chlorine, the mean values of resistance depended on the temperature (Table I). At 75° C resistance was decreasing from − 2.64% to − 3.45% after 27 and 53 days of exposure, respectively. At 135° C the decrease of resistance was − 3.52% after 27 days of exposure and − 3.05% after 53 days of exposure. At 175° C the decrease of resistance was − 4.10% after 27 days of exposure, then after 53 days of exposure became − 3.65%.

When observed changes of resistance were statistically checked by the paired t-tests, the changes after 27 days of exposure were significant for all three temperatures of exposure, with $p = 0.05$ for 75° C, $p = 0.025$ for 135° C and $p = 0.01$ for 175° C. The changes of resistance between the 27th and 53rd day of exposure were not significant for the samples exposed to 75° C.

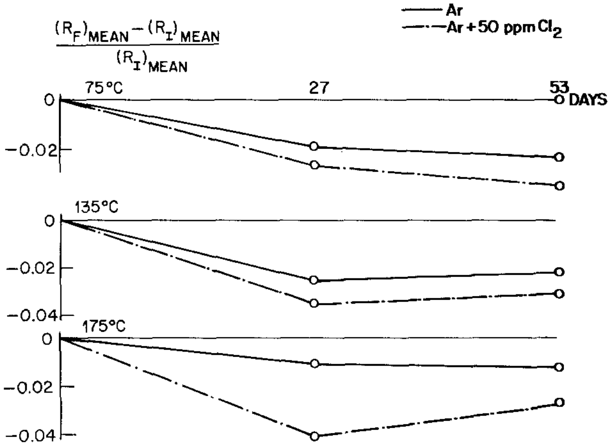

Figure 2 Experimental data for six chips tested at 75, 135 and 175° C in argon atmosphere and in argon plus 50 ppm chlorine atmosphere, respectively.

There was no change of resistance for the samples exposed at 135° C. For the samples exposed at 175° C, the resistance was increasing, with the mean difference significant only at $p = 0.1$.

2.2. Auger study of the effect of chlorine on gold–titanium metallization

The Auger analysis was performed on a Physical Electronics Industries Model 545 scanning Auger microprobe with a primary electron beam energy of 5 keV, beam diameter of approximately 5 μm and a modulation voltage of 2 eV. Other parameters such as beam current, sweep speeds, time constants, etc., were varied as required. Sputtering was done with 2 kV argon ions.

As a reference, one sample was analysed prior to any treatment. The Auger spectrum showed only carbon and oxygen in addition to the gold lines. Titanium and chlorine were not detected. Auger energy scans were run on representative areas of exposed samples for 53 days in six chips. A tabulation of elements detected is given in Table II. The intensity ratings are admittedly subjective and only suitable for a rough comparison. Absorbed electron scanning images as well as two-dimensional Auger images were made to describe surface topography and elemental distributions of selected areas.

After removing surface contamination by sputtering with 2 kV argon ions, results of the experiments at 135 and 175° C indicate that where chlorine was used, titanium came through the gold film in localized areas approximately 100 μm diameter (Samples 1 and 2, Table II and Fig. 3). The oxygen image coincides with the titanium indicating the titanium is present as an oxide. In the case of Samples 1 and 2, titanium was also found covering large areas of the gold surface between these spots, but depth profiling proved the oxide in these areas to be only a relatively thin layer approximately 100 to 200 Å thick.

Chlorine was generally found in these titanium-rich areas but only on the surface. After removal of just a few monolayers, no chlorine could be found in the titanium-rich areas.

One area shown in Fig. 4 gives clear evidence that although a high concentration of chlorine remains after some sputtering, its location is not directly superimposed on the titanium and oxygen but is immediately adjacent to it.

TABLE II Relative intensities of scanning Auger microprobe

Temperature (° C)	Sample no.	Atmosphere	Gold	Chlorine	Titanium	Oxygen	Carbon	Sulphur	Silicon
175	1	Ar-50 ppm Cl$_2$	1	3	4	4	2	nd	3
135	2	Ar-50 ppm Cl$_2$	3	4	5	4	4	2	2
75	3	Ar-50 ppm Cl$_2$	4	1	2	3	4	3	2
175	4	Argon	4	1	2	3	4	3	2
135	5	Argon	4	2	2	5	4	4	3
75	6	Argon	4	1	1	3	5	2	2

Intensity rating: nd, not detectable; 1, very weak; 2, weak; 3, medium; 4, strong; 5, very strong.

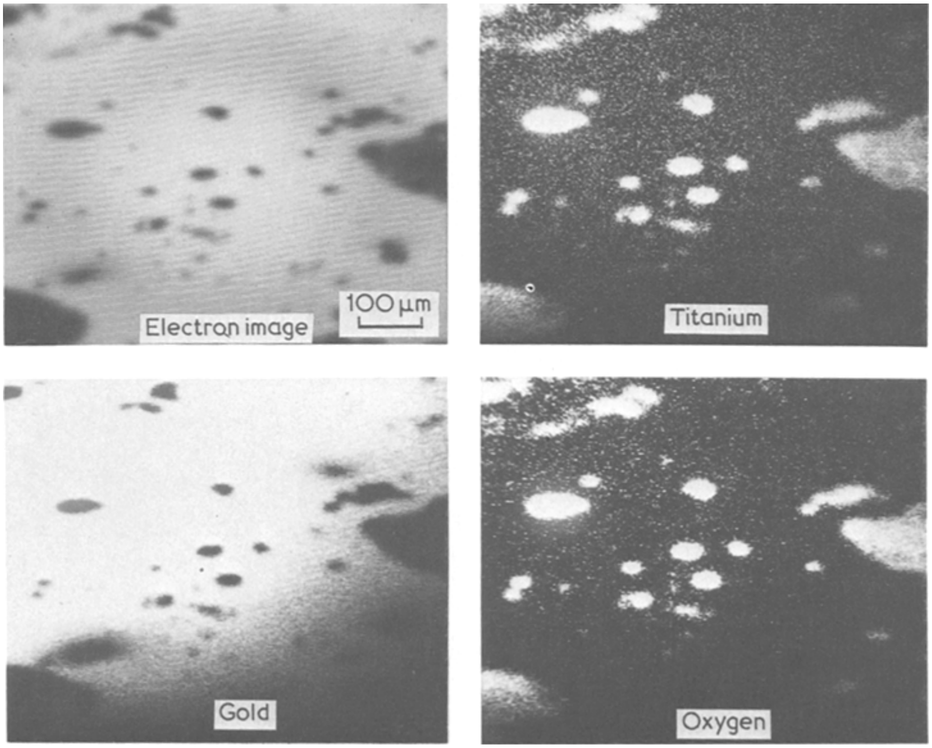

Figure 3 Auger scanning images of sample 2 (Table II), exposed at 135° C for 53 days to argon plus 50 ppm chlorine atmosphere, and after removing surface contamination by 2 kV argon ions.

2.3. X-ray study of the effect of chlorine and temperature on gold–titanium metallization

X-ray diffraction photographs of the Au–Ti thin films were taken with a high resolution Huber thin-field powder camera with monochromatic Cu$K\alpha_1$ radiation (Table III, Fig. 5). The reflections of the 5000 Å Au film were observed, but none of the underlying 750 Å Ti film. The X-ray patterns of the Au–Ti films exposed at 75 and 135° C look much alike and the presence of Cl_2 in the argon atmosphere does not result in any drastic change in the intensities. The X-ray patterns of the Au–Ti films exposed at 175° C, although much alike with or without the presence of Cl_2, now show a considerable change in intensities compared to the films exposed at lower temperatures. The main difference is that the 2 2 0, 2 2 2 and 4 0 0 reflections are considerably weaker (Fig. 5, Table III). If the X-ray intensities of all the exposed Ti–Au

TABLE III X-ray diffraction patterns estimated intensities of Au–Ti thin film

h k l	Sample Au Powder	Unannealed Ti–Au film	75° C		135° C		175° C	
			Ar	Ar + 50 ppm Cl_2	Ar	Ar + 50 ppm Cl_2	Ar	Ar + 50 ppm Cl_2
1 1 1	vs	vs	vs	vs	vs	vs	vs	vs
2 0 0	s	s	s	s	vs	ms	ms	ms
2 2 0	s	vs	vs	vs	s	vs	m	m
3 1 1	s	vs	ms	s	vs	ms	s	ms
2 2 2	m	m	mw	mw	mw	mw	vvw	vw
4 0 0	m	m	m	m	mw	m	vvw	vw
3 3 1	ms	s	ms	s	s	ms	ms	m
4 2 0	s	ms	m	m	m	m	mw	m
4 2 2	s	vs	vs	vs	vs	s	ms	ms

Intensity rating: vvw, very, very weak; vw, very weak; w, weak; mw, medium weak; m, medium; ms, medium strong; s, strong.

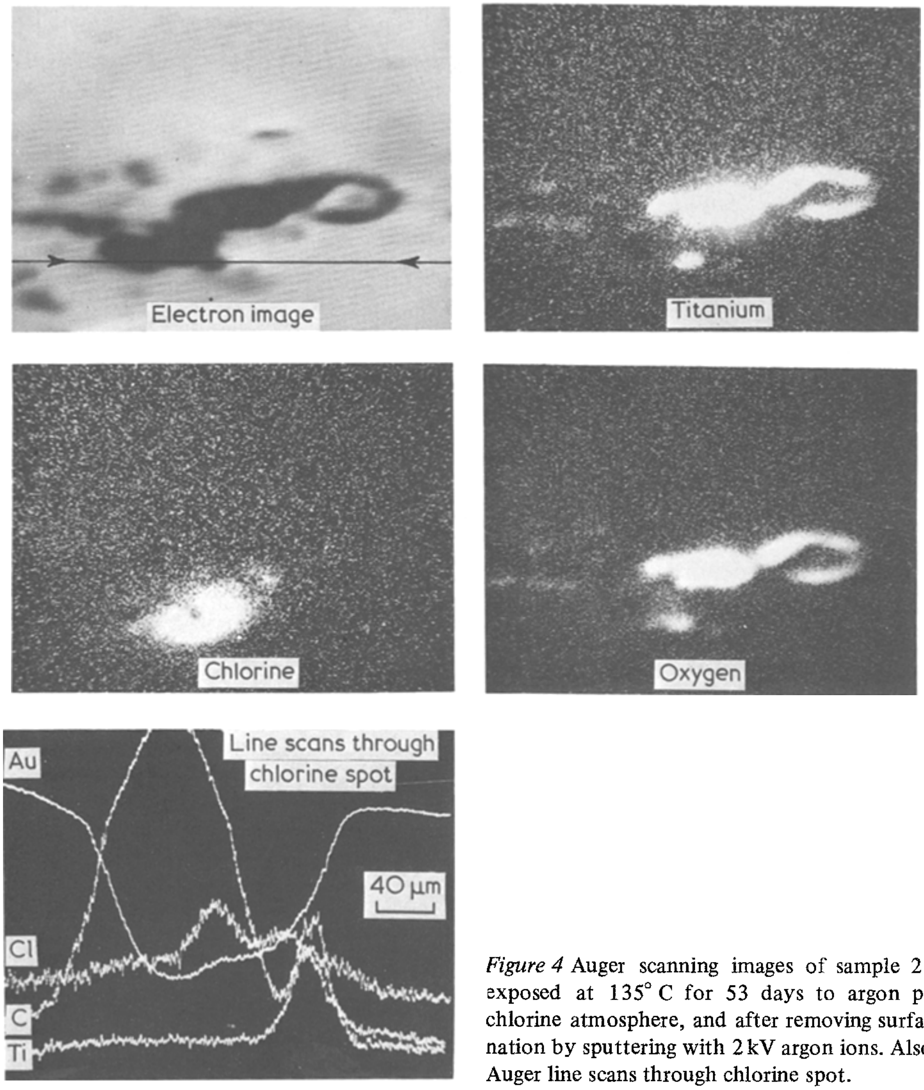

Figure 4 Auger scanning images of sample 2 (Table II), exposed at 135° C for 53 days to argon plus 50 ppm chlorine atmosphere, and after removing surface contamination by sputtering with 2 kV argon ions. Also shown are Auger line scans through chlorine spot.

samples are compared with those of an unexposed Au–Ti film or a randomly orientated Au powder (Fig. 5, Table III), the four Au–Ti samples exposed at lower temperatures look much the same as those of the unexposed Au–Ti samples or Au powder. This indicates that in these films the Au grains are more or less randomly orientated, while in the 175° C films the Au shows preferred orientation.

3. Discussion

Observations obtained in the present study suggest that a number of processes occur simultaneously in the gold layer during exposure of the samples to the argon atmosphere. These processes affect the physical properties of the gold layer in the samples. They developed the preferred orientation of the gold layer and changed the resistance of the samples. It seems that oxidation, annealing, migration and diffusion of the titanium atoms take place in the samples.

Diffusion is defined in this study as the process of transport of titanium atoms from the titanium layer to the gold layers. Migration of titanium atoms from the gold layer to the surface of the sample is considered as a separate independent process and is differentiated from the diffusion. Annealing is used in a general meaning of the term as coagulation of dislocations and vacancies and an increase in the preferred orientation of polycrystalline gold layer.

In the samples used in this study, the interfaces between titanium and gold layer were well defined. This was confirmed by the Auger spectroscopy.

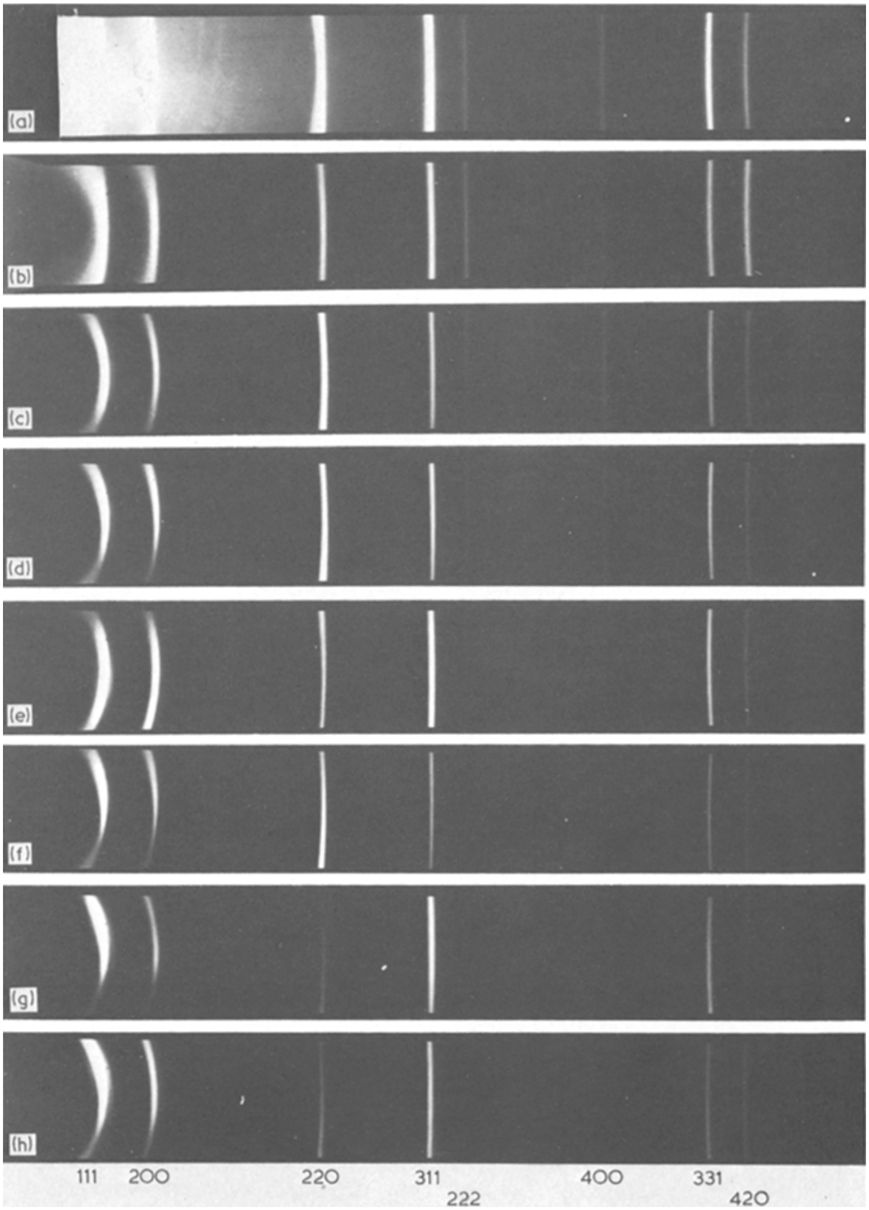

Figure 5 X-ray diffraction photographs of: (a) Au–Ti powder, (b) unannealed Au–Ti film, (c) sample exposed for 53 days at 75° C to the argon atmosphere, (d) sample exposed for 53 days at 75° C to the argon plus 50 ppm chlorine atmosphere, (e) sample exposed for 53 days at 135° C to the argon atmosphere, (f) sample exposed for 53 days at 135° C to the argon plus 50 ppm chlorine atmosphere, (g) sample exposed for 53 days at 175° C to the argon atmosphere, (h) sample exposed for 53 days at 175° C to the argon plus 50 ppm chlorine atmosphere.

With different atomic structures (face-centred cubic of gold and close-packed of titanium), different lattice constants (4.0788 Å for gold and 2.9050 Å for titanium) and different thermal coefficients of expansion ($\alpha = 14.2 \times 10^{-6}$ for gold and $\alpha = 8.4 \times 10^{-6}$ for titanium), large stresses are introduced at the interface, specially during the time of cooling, after deposition of the gold layer on the titanium layer, and an extremely large number of dislocations (up to 10^{12} dislocations cm^{-2}) are formed at the interface.

During deposition of gold, the temperature of the gold layer can be as high as 200° C and it can be expected that in these conditions a considerable number of titanium atoms diffuse into the gold layer along grain boundaries and dislocations.

Annealing, migration and diffusion are time- and temperature-dependent processes. It can be assumed that the rates of annealing, migration and diffusion decrease with time of exposure, while their rates increase with increasing temperature. Annealing and migration result in a decrease of resistance of the sample. Diffusion of titanium into the gold layer results in an increase of resistance of the sample.

Exposure of the samples to the tested range of temperatures and the addition of chlorine to the argon atmosphere has a noticeable effect on the resistance of the samples. In all tests, resistance of the exposed samples decreased and the addition of chlorine make this decrease even larger (Table I, Fig. 2).

Resistance of the titanium layers is order of magnitude larger than of the gold layer. It can be accepted, with only a negligible error, that resistance of the samples depends on the resistance of the gold layer only.

In samples exposed to the pure argon atmosphere during exposure of the samples to 75° C, the resistance of the samples decreased (Table I, Fig. 2). Changes observed in the samples' resistance can be attributed to the annealing of the gold layer of the sample.

An addition of 50 ppm of chlorine gas to the argon atmosphere causes an even larger decrease in the resistance of the samples. The effect of chlorine is related to the accelerated migration of titanium atoms from the gold layer to the external surface of the sample and is caused by chemisorption-induced segregation.

The effect of chemisorption-induced segregation in metals exposed to oxygen and hydrogen was established recently. Bouwman *et al.* [4], in an alloy of platinum and tin (PtSn and Pt_3Sn) observed oxygen-induced segregation by bringing tin to the surface of the sample. Hydrogen reduction of the surface, at 500° C, enriched the surface with platinum relative to the annealed state. Szymerska and Lipski [5] observed chemisorption-induced segregation of sulphur to the surface of paladium samples when exposed to hydrogen atmosphere. The effect of oxygen and hydrogen on the Pd–Au alloy was investigated by Mair *et al.* [6], and they reported a significant Pd surface enrichment due to oxygen chemisorption. The surface concentration of paladium increased further, when after oxygen treatment, the sample was exposed to hydrogen chemisorption. Similar to Szymerska and Lipski's [5] results, Bernasek and Staudt [7] studied chemisorption-induced segregation of sulphur by hydrogen from a molybdenum surface. In all these cases the acting agents were oxygen and hydrogen. In this investigation a new (third) acting agent, chlorine, was identified, which acted on the titanium present in the gold matrix.

At a temperature of 135° C, the pattern of behaviour changes. In the samples exposed to the pure argon atmosphere, some time between the 27th and 53rd day of exposure the decrease in the resistance reached its plateau (minimum resistance) and then remained constant. In the samples exposed to the argon atmosphere containing an additional 50 ppm chlorine, the resistance of the samples decreased up to 27 days exposure and then showed a tendency to increase (Table II).

In contrast to the pure argon atmosphere, samples exposed to the atmosphere containing chlorine and investigated by the Auger technique showed striking changes in the Auger spectrum as well as in the electron scanning images (Figs. 3 and 4). Samples exposed to the atmosphere containing chlorine at 75° C showed only traces of titanium and chlorine (Fig. 6a). In samples exposed at 135° C to the atmosphere containing chlorine, the Auger spectrum showed strong lines of chlorine and titanium (Fig. 6b). In the selected areas on the surface of the samples, titanium appeared in the form of platelets about 100 μm diameter and the external surface of these platelets was an oxide 100 to 200 Å thick.

The addition of chlorine to the argon atmosphere greatly enhances the migration of titanium through gold films. Careful examination of samples heated in the presence of chlorine showed a definite tendency for the titanium to move through the gold film in localized areas. The size and number of these areas increased with temperature and became massive at 175° C and produced violent eruptions on the gold surface (Fig. 7). In some areas funnels were formed leading to the glass substrate. The size and number of titanium platelets also would suggest that localized defects such as a pinhole or a concentration of grain-boundary intersections were the origin of these platelets. This is in agreement with previous observations that in gold–titanium metallizations, diffusion and migration of titanium through the gold layer occurred at the grain boundaries [2].

Since no similar areas could be found on any

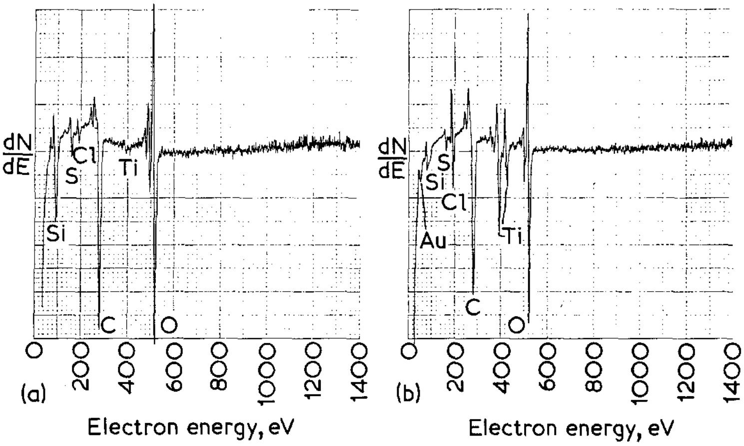

Figure 6 (a) Auger spectra of sample 3 (Table II), exposed for 53 days at 75° C to the argon plus 50 ppm chlorine atmosphere. Only traces of chlorine and titanium are visible in the spectrum. (b) Auger spectrum of sample 3 (Table II), exposed for 53 days at 135° C to the argon plus 50 ppm chlorine atmosphere. Very strong lines of chlorine and titanium are visible in the spectrum.

of the samples not exposed to chlorine, it must be concluded that chlorine plays a significant role in the migration mechanism. No evidence can be found to support the direct chemical combination of chlorine with titanium or its oxide (Fig. 4), but its presence in the same general areas suggests some activity within the gold grain boundaries that enhance the movement of titanium. It is reasonable to believe that this effect occurs in the grain boundaries in general, but the beam size of SAM of approximately 5 μm makes it incapable of resolving such individual boundaries. However, it does resolve those places where concentrations of these effects create larger areas.

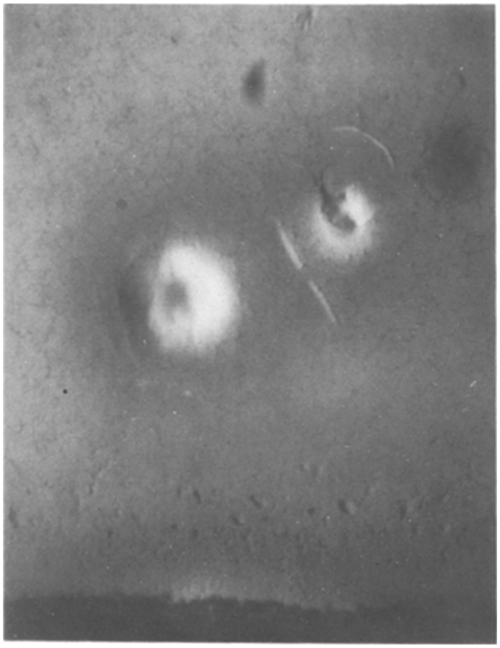

Figure 7 Disturbances on the gold layer surface are visible. These disturbances are formed by titanium brought to the surface through the gold layer. The sample was exposed for 53 days at 175° C to the argon plus 50 ppm chlorine atmosphere.

In previous investigations [2], diffusion of titanium through grain boundaries of the gold layer were clearly observed.

When samples were exposed to the pure argon atmosphere at 175° C, the resistance became approximately constant before the 27th day of exposure (Fig. 2, Table I).

This stability of the resistance can be related to the observed formation of the preferred oriented structure in the gold layer of the samples. In the initial stage (before 27 days exposure) a fast annealing and diffusion should be expected. Since their effect on the resistance of the samples is opposite, comparatively small changes in resistance were observed. In the later stage, a preferred oriented structure was developed, preventing or hampering both diffusion and the already partly completed annealing processes, and the resistance became nearly constant.

When samples were exposed to the pure argon atmosphere, at temperatures up to 175° C, migration of titanium atoms to the external surface of the samples was not observed. At 175° C the addition of the chlorine gas to the argon atmosphere has a very strong effect on the resistance of the samples. Initially, resistance decreased to the lowest observed value (− 4.11%), but after the 27th day of exposure began to rise (− 3.65%).

It is proposed here that at this temperature the effect of chlorine on diffusion of titanium was so strong that in spite of the formation of the preferred oriented structure, titanium atoms began to diffuse into the gold layer and the resistance started to increase.

It was noticed that simultaneous with the change in the intensities of the Au–Ti films exposed at 175° C, there was a considerable difference in resistivity change, ΔR, compared to the Au–Ti films annealed at lower temperatures. In the Au–Ti film annealed for 27 h at 175° C in pure argon, the resistivity change ΔR is much smaller than in films annealed at lower temperatures (– 1.04% at 175° C against – 2.47% at 135° C). This indicates that the resistivity is larger for the film annealed at 175° C and therefore more Ti seems to be present in this gold layer than in the gold layer of Au–Ti films annealed at lower temperatures. This means that at the highest temperature, 175° C, more Ti of the underlying Ti layer is diffusing into the Au layer.

This observation applies also to the samples exposed for 53 days in the pure argon atmosphere (Table I). In the samples exposed to the atmosphere containing chlorine, migration induced by chlorine is very strong. Its effect is stronger than that of diffusion and with increasing temperature of exposure, the resistance of the samples decreased (Table I).

4. Conclusions

In the experiments conducted in this study, a number of processes were observed. Depending on the conditions, annealing, diffusion, migration of the titanium atoms, and formation of the preferred oriented structure took place.

An addition of 50 ppm chlorine gas to the argon atmosphere at higher temperatures (135 and 175° C) had a pronounced effect on the migration of titanium atoms which affected the resistance of the samples A very active migration of the titanium atoms from the gold layer to the external surface of the samples was observed. Platelets of titanium on the external surfaces were formed and extended with increase in temperature. At some points (probably at the intersections of grain boundaries), migration of titanium atoms was so active that funnels in the films were formed extending up to the glass substrate. It should be emphasized that at the temperatures and times of exposure used in this study, migration of titanium atoms and formation of the platelets on the samples' surface were not observed in the samples exposed to the pure argon atmosphere. This strongly suggests that chlorine acts as an agent in chemisorption-induced segregation bringing titanium to the surface of the gold layer. On the surface titanium forms an oxide, but does not form any alloy with chlorine or gold. Judging by the appearance of the titanium deposited on the external surface of the samples and previous observations [2], migration of titanium occurs along grain boundaries, and from there spreads to the surface of the sample.

Since the resistance of titanium layers was orders of magnitude larger than the resistance of the gold layers, it can be accepted with only a negligible error that the resistance of the samples depended on the resistance of the gold layer.

The resistance of the gold–titanium thin film decreases when exposed at 75 and 135° C to the pure argon atmosphere, as was observed previously [2]. The observed decrease of resistance is attributed to the annealing of the lattice imperfections in the gold layer. With increase in temperature of exposure to 175° C, the decrease of resistance becomes smaller. At this temperature diffusion of titanium into the gold layer is initiated.

When samples were exposed at 175° C, titanium began to diffuse into the gold layer and the resistance began to increase. But even before the 27th day of exposure a preferred oriented structure in the gold layer was developed. Formation of the preferred oriented structure apparently prevented diffusion of titanium into the gold layer and resistance became constant. Formation of the preferred oriented structure was not conditioned or related to the presence of chlorine in the atmosphere.

The significant decrease of resistance in samples exposed to the atmosphere containing chlorine in addition to argon, compared to the atmosphere containing only pure argon, can be attributed to the decrease in resistance of the gold layer. This decrease of resistance results from the migration of titanium atoms from the gold layer to the external surface of the sample, with chlorine acting as an agent in chemisorption-induced segregation, and the decreasing density of titanium in the gold layer.

Acknowledgements

The authors would like to express gratitude to Drs H. Schreiber Jr and J. M. Vandenberg from

Bell Laboratories, Murray Hill, New Jersey, for their contribution to this work. Dr Schreiber performed all work connected with Auger study and Dr Vandenberg that with the X-ray investigation.

References

1. A. T. ENGLISH and P. A. TURNER, *J. Electron. Mater.* **1** (1972) 1.
2. W. D. SYLWESTROWICZ, G. W. KAMMLOTT and H. A. ELKHOLY, *J. Mater. Sci.* **14** (1979) 873.
3. GEORGE W. SNEDECOR, "Statistical Methods", 5th edn. (Iowa State College Press, Ames, Iowa, 1956) p. 50.
4. R. BOUWMAN, L. H. TONEMAN and A. A. HOLSCHER, *Surface Sci.* **35** (1973) 8.
5. I. SZYMERSKA and M. LIPSKI, *J. Catalysis* **41** (1976) 197.
6. G. MAIRE, L. HILAIRE, P. LEGARE, F. G. GAULT and A. O'CINNEIDE, *ibid* **44** (1976) 293.
7. STEVEN L. BERNASEK and GLENN E. STAUDT, *ibid* **45** (1976) 372.

Received 22 September 1978 and accepted 28 June 1979.