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Effects of temperature, thickness and atmosphere on mixing in Au–Ti bilayer thin films

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The interdiffusion and intermetallic compound formation of Au–Ti bilayer thin films annealed at 125 to 350 °C have been investigated. The bilayer thin films were prepared through electron beam deposition at comparatively low temperature. The interdiffusion of annealed specimens was examined by measuring electrical resistance and the depth–composition profile, and by observation using a transmission electron microscope. Interdiffusion between the thin films was detected at temperature above 175 °C in a vacuum of 10^{-4} Pa. The starting temperature at which interdiffusion occurred decreases with lowering annealing vacuum. The intermetallic compounds AuTi, Au_4Ti, Au_2Ti and Ti_3Au form during annealing at over 250 °C. The activation energies of Au in Ti and Ti in Au obtained by the penetration depth are approximately 0.45 and 0.41 eV, respectively. These measurements indicate that the diffusion is controlled by a short-circuit mechanism. The diffusion of Ti species in Au depends on the annealing vacuum and Au thickness.

1. Introduction

Gold–titanium bilayer thin film is of interest for its potential as a wiring material for semiconductor and other devices [1–8]. This system forms several intermetallic compounds as shown in the equilibrium phase diagram [9] and confirmed in thin film experiments [1–5]. $TiAu_2$, TiAu and Ti_3Au compounds form during deposition at a substrate temperature of 150 °C and the formed compound particles grow during subsequent annealing [1]. Hieber [6], however, confirmed that interdiffusion between Au and Ti occurs at 207 °C. From diffusion results during annealing at 250–450 °C, Dhere and Patnaik [5] estimated that the safe operating temperature for the Au–Ti system is 150 °C or less. Short-circuit diffusion along grain boundaries was proposed as a diffusion mechanism which causes intermetallic compounds to form along the grain boundaries [1–4]. The temperature at which interdiffusion between the films begins, however, is unclear.

This paper describes the interdiffusion between gold and titanium thin films at relatively low temperatures, and the impact of the Au film thickness and annealing vacuum.

2. Experimental procedure

Au–Ti bilayer thin films were prepared by conventional electron beam deposition in a vacuum of 0.7×10^{-4} Pa. The source material purities were 99.99 wt % for Au and 99.95 wt % for Ti. The substrate, Corning No. 7059 glass, was heated at 200 °C for Ti evaporation and to 50 °C for Au evaporation. The gold deposition temperature was selected to prevent the films reacting together before annealing. The film thicknesses were 50 to 150 nm for Ti and 30 to 300 nm for Au. The bilayer thin films were annealed for 1 to 3 h under 10^{-4} to 10^{-2} Pa, at 125 to 350 °C.

The electrical resistance of the bilayer thin films was measured using a four-probe method. Depth–composition profiles were obtained by means of Auger electron spectroscopy (AES). The cross-sectional microstructure was observed using a transmission electron microscope (TEM). The observed specimen was prepared by abrading the substrate and then finally thinned by ion etching.

3. Results and discussion

3.1. Electrical resistance

The changes in electrical resistance for Au (30 nm thick)–Ti (150 nm thick) bilayer thin film annealed under 10^{-4} Pa are shown in Fig. 1. Resistance change is first observed at 175 °C, and the value increases with the annealing temperature. The electrical resistances of the above Au and Ti single-layer films do not obviously increase at 175 °C. The resistance increase in bilayer thin films is therefore attributed to interdiffusion between the Au and Ti layers. Since the Au layer resistivity is much lower than that of the Ti layer, the resistance change is very sensitive to the thickness of the Au layer. The temperature at which the resistance change begins apparently increases with an increase in the Au layer thickness. This does not, however, mean an increase in the starting temperature for the interdiffusion between the films. The starting temperature is slightly higher than that estimated [2] and lower than that of the previous experiment [6].

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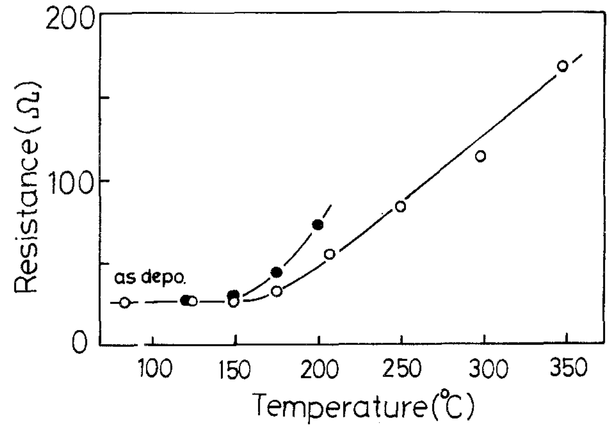

Figure 1 Effect of annealing temperature on the electrical resistance of Au–Ti bilayer thin film. The film thicknesses are 30 nm for Au and 150 nm for Ti; they were annealed in (○) 10^{-4} and (●) 10^{-2} Pa.

3.2. Depth–composition profile

Depth–composition profiles for Au (30 nm thick)–Ti (150 nm thick) bilayer thin film are shown in Fig. 2. Although no clear profile change was detected in the specimens after annealing below 150 °C under 10^{-4}Pa, the profile changed slightly after annealing at 175 °C for 2 h. This agreed with the results of electrical resistance measurement. The profiles after annealing at 225 °C, for 2 h were very different. The Ti species migrated to near the Au film surface. After annealing at 250 °C for 2 h, the Ti species was enriched near the Au surface, possibly due to the oxygen in the atmosphere. This is discussed later.

No enrichment of the Ti species was observed near the Au surface of Au (150 nm)–Ti (100 nm) bilayer thin films. This is due to the thickness of the Au layer. The logarithmic depth versus inverse temperature plot is linear . The activation energy obtained from the relationship was approximately 0.45 eV for Au in the Ti layer. Similarly the activation energy of Ti species in the Au layer was 0.41 eV. These values are very small, indicating that the species migrates along a short-circuit path such as a grain boundary.

The depth–composition profiles of Au (150 nm)–Ti (150 nm) bilayer film annealed at 300 °C for 3 h are shown in Fig. 3. A peak near the surface and a midway hill can be detected in the Ti content, and a small peak near the surface and three steps in the Au content. It is thought that the peaks and steps show the effect of the annealing atmosphere and the intermetallic compound formation, respectively.

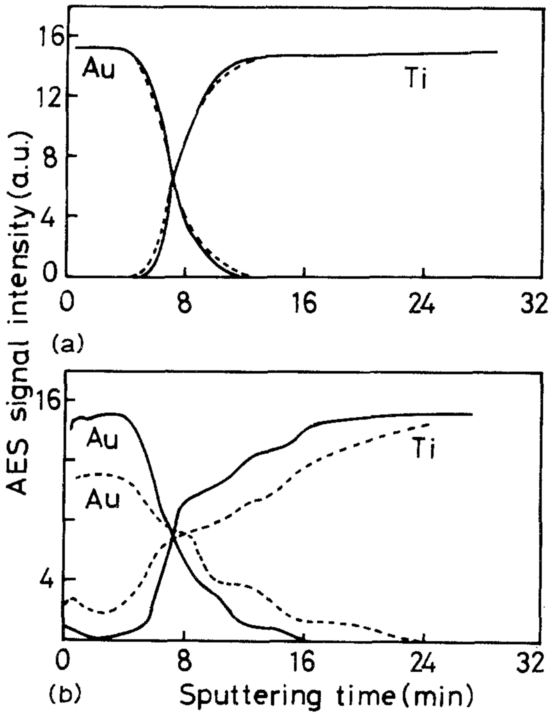

Figure 2 Depth–composition profiles of Au–Ti bilayer thin film: (a) as (——) deposited and (– – –) annealed at 175 °C, and (b) annealed at (——) 225 and (– – –) 250 °C, in 10^{-4} Pa.

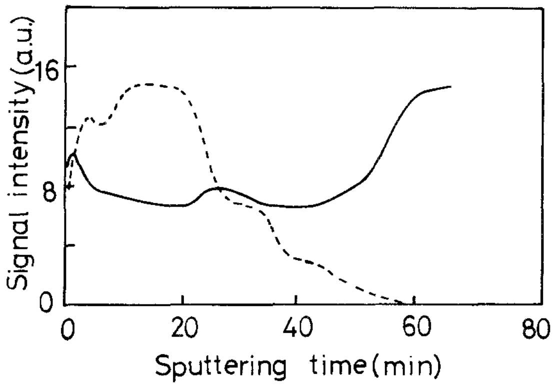

Figure 3 Depth–composition profiles of Au (150 nm) –Ti (150 nm) bilayer thin films, annealed at 300 °C in 10^{-4} Pa: (– – –) Au, (——) Ti.

3.3. Intermetallic compounds

The annealed specimens were examined by X-ray and electron diffractometry. The identified intermetallic compounds are shown in Table I. No intermetallic compound was identified following annealing below

TABLE I Compounds detected by X-ray diffractometry

Compound	Au (30)–Ti (150)[a]				Au (200)–Ti(50)				Au (150)–Ti(150)	
	200 °C	225 °C	250 °C	280 °C	200 °C	225 °C	250 °C	280 °C	250 °C	300 °C
Au_4Ti	–	–	–	–	–	–	0	0	–	?
Au_2Ti	–	–	?	?	–	?	0	–	0	0
AuTi	–	?	0	0	–	–	–	–	0	0
Ti_3Au	–	–	?	0	–	–	–	–	–	?

[a] Figures in brackets represent film thickness (nm).

225 °C. Although intermetallic compounds were formed after annealing at over 250 °C, the concentrations of the compounds formed were affected by the thickness of Au and Ti layers. It is thought that this is due to the change of thermodynamic condition of the thin film system. For example, AuTi and Ti_3Au were formed for Au (30 nm thick)–Ti (150 nm thick), while Au_4Ti and Au_2Ti were identified in the Au (200 nm thick)–Ti (50 nm thick) specimen. These results indicate that the composition of the intermetallic compound formed is dominated by the thicker metal layer in the bilayer thin film.

In the bilayer thin films, interfaces between the bilayer thin films and substrate–metal-film interfaces have high energy. The effects of surface energy and internal stress of the film are also strong. The thermodynamic equilibrium condition of the bilayer thin film system is therefore affected by the thicknesses of the films. It is thought that such thermodynamic changes are the cause of different intermetallic compound formations. Oxygen in the atmosphere is also thought to influence the thermodynamic condition.

3.4. Microstructural change

Cross-sectional transmission electron micrographs of as-deposited and annealed Au–Ti bilayer thin films are shown in Fig. 4. Both Au and Ti films were 50 nm thick. No change in microstructure was observed between the Au and Ti layers before or after annealing below 200 °C, but a slight microstructural change was observed in the specimen after annealing at 225 °C.

The surface shape observed by using TEM changed from smooth to rough. A typical cross-sectional electron micrograph of the specimen, annealed at 250 °C, is shown in Fig. 4b. The intermetallic compounds were detected by X-ray diffractometry of the specimen. Although a degenerative layer was observed, TEM did not show any obvious image of the compounds. The arrows in the figure indicate dents near the Au surface. These dents are probably caused by preferential diffusion of Au species from the Au to the Ti layer or by the formation of intermetallic compounds. If the dents near the Au surface are formed by Kirkendall diffusion, vacancies must migrate from the Ti layer toward the Au layer. As the vacancies were not supplied from the substrate side, the supply channel for vacancies to make the dents is not obvious.

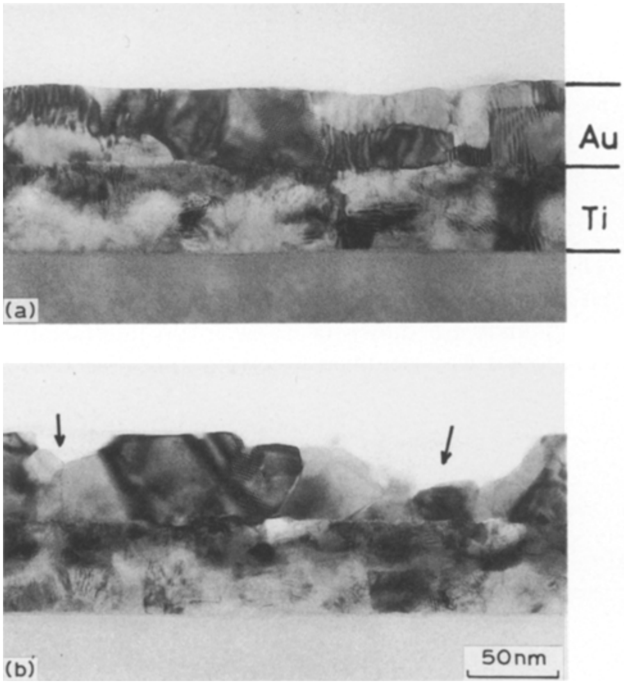

Figure 4 Cross-sectional transmission electron micrographs of bilayer film (a) as deposited and (b) annealed at 250 °C in 10^{-4} Pa.

3.5. Effect of annealing vacuum

Since there is a strong chemical affinity between Ti and oxygen, the influence of the annealing atmosphere on Ti diffusion in the Au film must be considered [10]. Distributions of Ti species in Au (50 nm)–Ti (150 nm) bilayer films annealed in different vacuums are shown in Fig. 5. The annealing was performed under 10^{-4} to 10^{-2} Pa, at 200 °C for 3 h. The diffusion distance of Ti in Au films increased with the annealing vacuum. The oxygen diffusion depth from the Au surface also increased with lowering annealing vacuum. The Ti species in the specimen annealed in a vacuum of 10^{-2} Pa, were enriched near the Au surface. These results show that the Ti–O affinity enhances the migration of Ti in the Au layer.

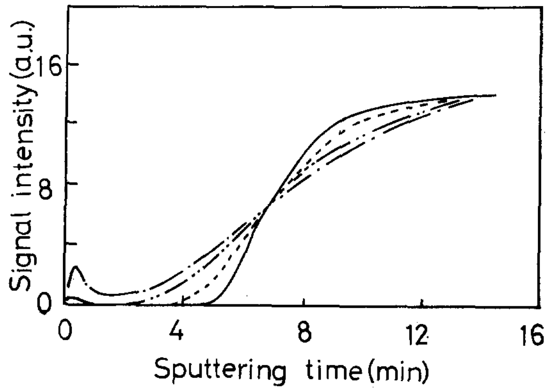

Figure 5 Effect of annealing atmosphere on depth–composition profiles of Au (50 nm)–Ti (150 nm) bilayer thin films (——) as deposited and annealed at 200 °C for 3 h in (– – –) 10^{-4}, (— - - —) 10^{-3} and (—·—) 10^{-2} Pa.

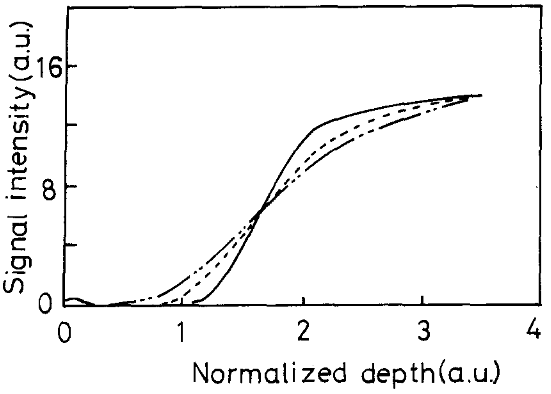

Figure 6 Effect of Au thickness on depth–composition profiles of Au–Ti bilayer thin films, annealed at 200 °C for 3 h in 10^{-3} Pa. Au thickness; (— - - —) 50 nm, (– – –) 100 nm, (——) 300 nm.

The diffusion depth of Ti changed as the Au thickness changed. Normalized distributions of the Au thickness dependence of Ti species are shown in Fig. 6. The annealing was performed in a vacuum of 10^{-3} Pa, at 200 °C for 3 h. The Ti depth profiles show a decrease in the diffusion depth of Ti species in the Au film as the Au film thickness increased. This indicates a decrease in the effective Ti–O affinity with increasing Au film thickness. The starting temperature of the interdiffusion did not increase. Sylwestrowicz and Elkholy [4] reported that water in an argon atmosphere does not affect the interdiffusion. It is thought that this is because the effective affinity between Ti and O is weak in the presence of a thick Au film and/or water.

4. Conclusions

Au and Ti thin films start to interdiffuse at 175 °C under 10^{-4} Pa. This may be due to short-circuit diffusion. Intermetallic compounds are formed during annealing at annealing temperatures above 250 °C. The intermetallic compounds formed depend upon the film thickness. The interdiffusion is affected by the annealing vacuum and bilayer film thickness.

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References

1. T. C. TISONE and J. DROBEK, *J. Vac. Sci. Technol.* **9** (1972) 271.
2. J. D. SPEIGHT and K. COOPER, *Thin Solid Films* **25** (1975) S31.
3. C. H. LING, *Phys. Status Solidi* (*a*) **80** (1983) K59.
4. W. D. SYLWESTROWICZ and H. A. ELKHOLY, *J. Mater. Sci.* **14** (1979) 873.
5. N. G. DHERE and B. K. PATNAIK, *Thin Solid Films* **85** (1981) 316.
6. H. HIEBER, *ibid.* **37** (1976) 335.
7. M. MURAKAMI and K. K. KIM, *J. Appl. Phys.* **56** (1984) 2076.
8. M. R. PLICHTA, H. I. AARONSON and J. H. PREPEZKO, *Acta Metall.* **26** (1978) 1293.
9. M. HANSEN, "Constitution of Binary Alloys" (MacGraw-Hill, New York, 1964).
10. M. KITADA and N. SHIMIZU, *J. Mater. Sci.* **19** (1984) 1339.

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