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Reaction of Al/Mo thin films

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Intermixing and compound formation by means of annealing have been studied for Al/Mo thin films. With annealing at 300° C, only intermixing between aluminium and molybdenum films occurs due to mutual diffusion. With annealing at over 350° C, $Al_{12}Mo$ and $AlMo_3$ compounds were formed. The electrical resistivity of the film increases with intermixing and compound formation. The electrical resistivity increase is proportional to the annealing time, $t^{1/2}$. In low vacuum annealing, molybdenum oxide film forms on aluminium film. It is assumed that molybdenum atoms diffuse through the aluminium film due to their chemical affinity with oxygen in the atmosphere.

1. Introduction

Aluminium thin film has been used as electrode and wiring materials for ICs, LSIs, planar type magnetic sensors, and other thin film devices. However, reactions between aluminium thin film and active layer materials often occur in such devices [1]. For this reason, certain high melting-point transition metals have been used as barrier films between aluminium thin films and the active materials. Molybdenum thin film is one such metal, and is used as a gate metal for silicon transistors [2]. In such a case, the molybdenum silicide layer prevents any reaction between the aluminium electrode and silicon active layer. However, Al/MoSi/Si is not stable above temperatures of 500° C [3], and the details of this phenomenon are not clear. Thus, in thsi work, the reaction between aluminium and molybdenum thin films has been studied with the view of clarifying the reaction mechanism.

2. Experimental details

Aluminium/molybdenum thin film specimens were prepared using a conventional electron beam deposition system under a vacuum of 2×10^{-6} torr. Source materials were 99.999% pure aluminium and 99.99% pure molybdenum. Corning No. 7059 glass, cloven NaCl, and carbon film vapour-deposited onto a mica sheet were used for the substrate. In the specimen preparation, molybdenum film was at first deposited onto substrates and then aluminium film was formed onto the molybdenum film in a continuous manner.

These specimens were annealed at 250 to 500° C for 0.5 to 6 h under a vacuum of 2×10^{-6} torr. To observe the influence of remaining oxygen in an annealing atmosphere, some specimens were annealed under a 10^{-3} to 10^{-4} torr vacuum.

Depth profile measurements were performed using an ion analyser, as well as Auger electron spectroscopy. Microstructures of the films were observed by means of an electron microscope.

3. Results and discussion

3.1. Microstructure

The microstructure of an as-deposited aluminium/molybdenum film is shown in Fig. 1a. The large aluminium grains indicated by the arrows in the figure and molybdenum fine grains were observed. From the electron diffraction pattern, it was recognized that aluminium and molybdenum did not react when as-deposited. Reactions like compound formation between aluminium and molybdenum were also not observed in the specimen after annealing at 300° C. Therefore, obvious microstructural changes were not observed. However, mutual diffusion did occur, as will be described in what follows.

The microstructure of the specimen after annealing at 350° C for 3 h is shown in Fig. 1b. Formation of the intermetallic compound $Al_{12}Mo$ [4] was identified from the electron diffraction

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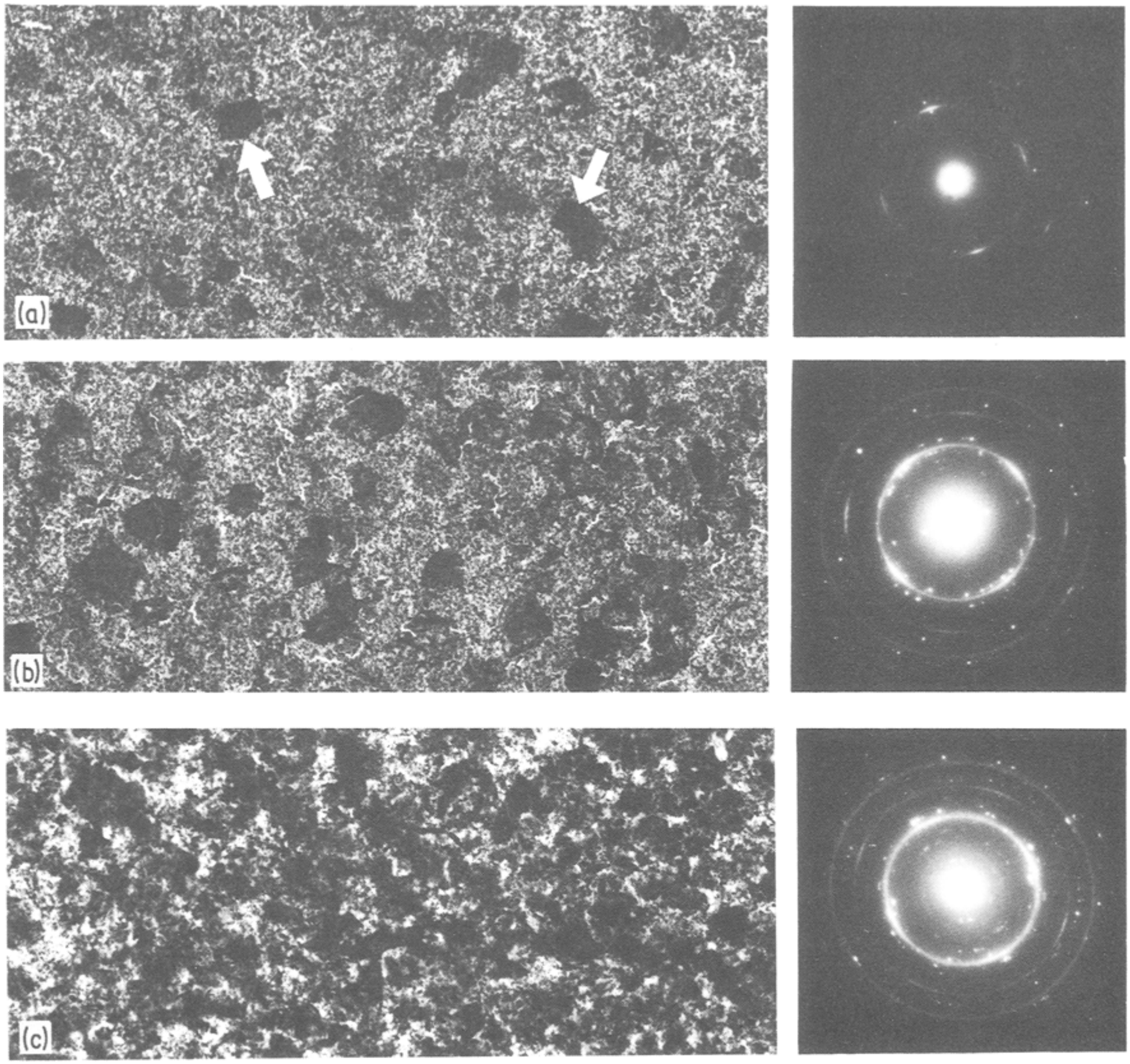

Figure 1 Transmission electron micrographs and electron diffraction patterns for aluminium/molybdenum thin films. (a) As-deposited, (b) annealed at 350° C for 3 h, (c) annealed at 450° C for 3 h.

pattern. After long annealing, though, no other intermetallic compounds were detected.

The microstructure of the specimen after annealing at 450° C for 3 h is shown in Fig. 1c. The microstructure was slightly changed. Molybdenum fine grains disappeared partly, and the observed molybdenum grains grew. Intermetallic compounds $Al_{12}Mo$ and $AlMo_3$ [4] were detected from the electron diffraction. After annealing at 500° C for 3 h, $Al_{12}Mo$, $AlMo_3$ and other electron diffraction spots from an unknown compound were detected. However, the details could not be clarified.

3.2. Depth composition profile

Depth composition profiles for as-deposited and annealed aluminium/molybdenum specimens are shown in Figs. 2 to 5. The deposited aluminium and molybdenum were both 50 nm in thickness. Depth profiles of the elements for the as-deposited specimen are shown in Fig. 2. From these profiles, however, the exact intermixing of the elements could not be determined because a profile shift occurred in analysing the method itself. It is considered, though, that the intermixing is very small, because the aluminium deposition temperature was sufficiently low (100° C).

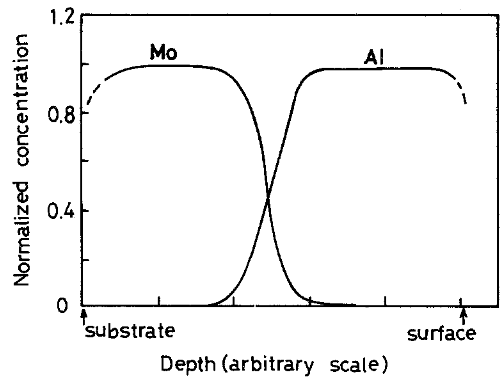

Figure 2 Depth composition profiles for as-deposited aluminium/molybdenum thin films.

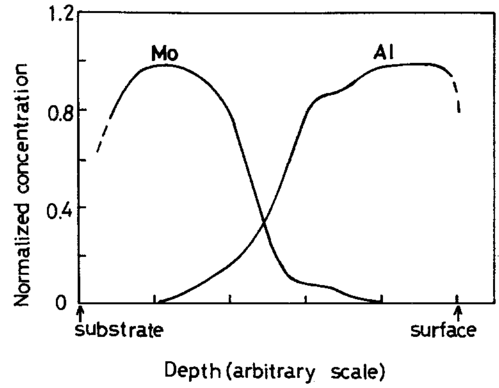

Figure 4 Depth composition profiles for aluminium/molybdenum film annealed at 350° C.

Depth composition profiles after annealing at 300° C for 3 h are shown in Fig. 3. In this state, obvious intermixing was detected in comparison with the depth profiles for the as-deposited specimen shown in Fig. 2. However, no discontinuity in the profile was observed. It is therefore considered that no intermetallic compound was formed with 300° C annealing. This result is in good agreement with those from electron microscopic observation.

Composition depth profiles for specimens annealed at 350° C for 3 h are shown in Fig. 4. The profiles showed compositional discontinuities in both aluminium and molybdenum. These existed in or near the aluminium film side. The relative atomic ratio of aluminium/molybdenum at this depth was about 10. In this layer, an intermetallic compound, $Al_{12}Mo$, was formed. In the specimen annealed at 450° C for 3 h, two discontinuities in the composition profiles were observed. This is shown in Fig. 5. The exact composition ratio for aluminium/molybdenum could not be determined because the profile was very complicated.

From the results of electron diffraction analysis, two intermetallic compounds were recognized. Therefore, this compositional profile could be seen to correspond to that for the compounds $Al_{12}Mo$ and $AlMo_3$. Electron diffraction from $Al_{12}Mo$ showed up as dot-like spots. From this and the depth profile, it is assumed that the compound grew like an epitaxial growth on aluminium grains. Therefore, it is considered that molybdenum atoms diffused into the aluminium crystal lattice. On the other hand, electron diffraction from the compound $AlMo_3$ was ring-like. Therefore, this $AlMo_3$ perhaps formed on the fine molybdenum grains.

3.3. Electrical resistivity

The electrical resistivity of aluminium/molybdenum thin film was measured to achieve a good reflection of the microstructural change in the film. Normalized electrical resistivities for

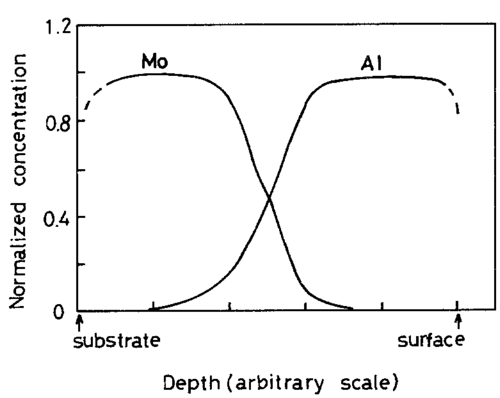

Figure 3 Depth composition profiles for aluminium/molybdenum film annealed at 300° C.

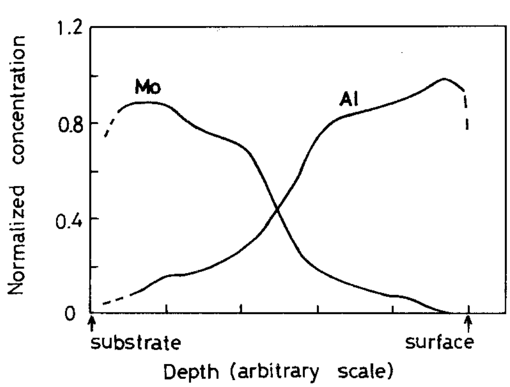

Figure 5 Depth composition profiles for aluminium/molybdenum film annealed at 450° C.

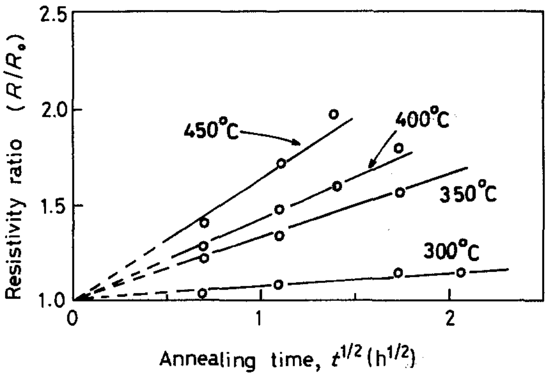

Figure 6 Electrical resistivity against annealing time for aluminium/molybdenum thin films: R_0 = as-deposited, R = annealed.

aluminium/molybdenum films having various annealing conditions are shown in Fig. 6. The resistivity for a specimen annealed at 250° C did not change. When the annealing temperature was higher than 300° C, the resistivity increased with increasing annealing time. Also, the resistivity increased rapidly with increasing annealing temperature. The increase in electrical resistivity was proportional to $t^{1/2}$ (t is the annealing time). This means that the compound formation process was controlled by element diffusion [5].

3.4. Effect of annealing vacuum

The depth composition profile for a specimen annealed at 450° C for 3 h in a vacuum of 10^{-3} torr

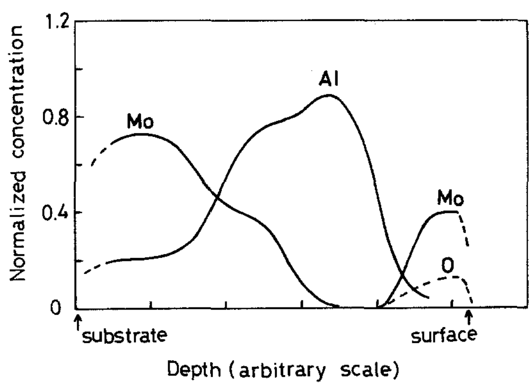

Figure 7 Depth composition profiles for aluminium/molybdenum film annealed at 450° C in a vacuum of 10^{-3} torr.

is shown in Fig. 7. In this profile, intermixing of aluminium and molybdenum was observed. Molybdenum, which diffused through the aluminium film, was also measured on the aluminium film. The molybdenum layer on the aluminium film had a purple-like interference colour. This means that the molybdenum was oxidized in an annealing atmosphere. In fact, oxygen was detected by the depth composition measurement, as Fig. 7 shows. Therefore, it is assumed that the molybdenum atoms diffused towards the aluminium surface due to chemical affinity with oxygen in the atmosphere. The molybdenum oxide film did not show a clear cyrstal structure on the electron diffraction pattern. Consequently, it is considered that the oxide film has a glass-like structure.

4. Conclusion

The intermixing and compound formation between aluminium and molybdenum thin film were recognized by annealing temperatures above 300 to 350° C. From the results of electron diffraction and depth composition profile analyses, the relation between the compounds formed and annealing temperature was clarified.

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References

1. E. PHILOSFKY and E. L. HALL, *IEEE Trans.* **PHP-11** (1975) 281.
2. T. MOCHIZUKI, K. SHIBATA, T. INOUE and K. OHUCHI, *Jpn. J. Appl. Phys.* **17** (1977) 37.
3. F. MOHAMMADI, Technical Rep. No. G503-1 (Integrated Circuit Laboratory Report, Stanford University, 1980) p. 33.
4. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
5. D. GUPTA and P. S. HO, *Thin Solid Films* **72** (1980) 399.

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