Pergamon

Scripta Materialia, Vol. 34, No. 9, pp. 1473-1477, 1996
Elsevier Science Ltd

1359-6462/96 $12.00 + .00

PII S1359-6462(96)00004-8

OBSERVATIONS OF GUINIER-PRESTON ZONES IN AN AS-DEPOSITED Al-1wt.%Si-0.5wt.%Cu THIN FILM

Chih-Hang Tung*, Re-Long Chiu**, and Peng-Heng Chang**
*Vanguard International Semiconductor Corp.,
Science Based Industrial Park, Hsinchu,
**Institutes of Materials Science and Engineering, National Chiao Tung University,
Hsinchu, Taiwan 300, R. O. C.

(Received August 11, 1995)
(Revised November 22, 1995)

Introduction

Aluminum-copper (Al-Cu) and Aluminum-silicon-copper (Al-Si-Cu) films are widely used as interconnects and contacts in contemporary very large scale integration (VLSI) technology. Cu alloying in Al results in the formation of intermetallic Al_2Cu precipitates, which increase corrosion susceptibility as well as process difficulty. Understanding the formation of Al2Cu theta-phase precipitates within Al alloy thin films is thus of great scientific and technical value. The precipitation behaviour of Al_2Cu theta-phase from a supersaturated Al matrix in Al-Cu and Al-Si-Cu alloys in bulk materials has been extensively studied(1,2). Precipitation proceeds via the following scheme:

$$\text{supersaturated solid solution} \rightarrow \text{GPI/II} \rightarrow \theta' \rightarrow \theta,$$

where GP I/II stands for Guinier-Preston zones. θ' is a metastable phase with tetragonal structure, θ is the equilibrium phase having a body-centered tetragonal structure. GP zones are small segregations formed by atomic redistribution over crystal lattice sites of the homogeneous solid solution. GP zones cannot be regarded as new phase precipitates because they do not have well-defined boundaries and their structure is continuously transformed into the parent phase structure. Experimentally GP zones in bulk Al-Cu alloys are always observed to lie on Al {100} planes(3.4).

The precipitation process in Al-Si alloys is much simpler than that of Al-Cu system. Particularly there is no intermetallic compound formation in the Al-Si system, the Al-rich terminal solid solution decomposing to pure Si and Al. Plates of Si on {111} planes are preferred morphology(5) but needle precipitates with axes lying along <100>, <110> and <113> directions are also found(5,6). The growth of semi-coherent {111} plates has been shown to occur initially by the coprecipitation of vacancies and Si atoms(5). The Si precipitates are well accommodated in the Al matrix in the later stages of growth and they are invariably twinned.

It is generally believed that GP zones do not exist in either Al-Cu or Al-Si-Cu thin films formed by normal metallization process of VLSI(7-12). Depending on the deposition and thermal history, most studies observed θ' and/or θ phases formed within aluminum grains or along grain boundaries, edges, and substrate interface. The absence of GP zones was attributed to the low excess vacancy density in thin films(8,11). However, in this paper experimental evidence is presented to show the existence of GP zones in an as-deposited Al-1%Si-0.5%Cu thin film.

Experimental Procedures

Four inch silicon wafers of <100> orientation were thermally oxidized to form a 550 nm thermal oxide followed by chemical vapor deposition of a 600 nm borophosphosilicate glass (BPSG) layer at 720°C. A 300 nm thick aluminum alloy film, was subsequently deposited in a Varian DC magnetron sputtering deposition machine from a target with the nominal composition of Al-1wt%Si-0.5wt%Cu under an argon atmosphere with a deposition rate of 21 nm/sec. Deposition was nominally carried out at room temperature, but the actual wafer temperature was approximately 100°C due to sputter heating. No subsequent heat treatment was carried out. Transmission electron microscopic (TEM) samples were prepared through normal sample preparation procedures(13). The highest temperature that the TEM samples ever experienced during sample preparation was about 150°C for no more than 3 minutes when the samples were placed on a hot plate. Final thinning was performed by ion milling from the substrate side at 4 KeV and 0.3mA in a Gatan 600 ion miller. The milling time was limited to less than 2 hours to avoid any ion bombardment artifacts. Conventional and high resolution TEM were performed respectively in Philips CM20 and JEOL 2000EX microscopes, both operating at 200 kV.

Results and Discussion

The as-deposited films were polygranular with grain size ranging approximately from 0.5 μm to 2.5 μm. Large and internally twinned silicon precipitates were observed and identified at the Al grain boundaries, an example is shown in Fig.1. Higher magnification imaging of the Al grain interior, Fig.2, shows discrete strain island contrasts. Lattice images from some of the grains are shown in Fig.3, and a typical diffraction pattern from these areas is shown in Fig.4. These micrographs were viewed along Al <110> direction and Al {111} lattice fringes with lattice spacing d_{111} = 0.234 nm are clearly resolved. High density of dark plates aligned along Al {111} with about two to four Al {111} planes thick and about 5 to 10 nm long can be observed. These plates, with dark strain fields around, are structurally coherent to the Al parent lattice without discernible boundary within the present resolution. Selected area diffraction pattern, Fig.4, shows streaks along <111> directions, characteristic of disk shaped precipitates lying on Al{111} planes. The characteristics of GP zones are clearly demonstrated in these high resolution images alongside the associated diffraction pattern(14). Attempts were made to identify the chemical nature of the precipitates by means of high resolution electron energy loss spectroscopy (EELS), but due to the resolution limit of our TEM the result is inconclusive. It is uncertain whether the observed GP zones are due to Si or Cu precipitation. If they are Si plates, it would be the first time that GP zones are observed to result from Si precipitation. The possibility of Si GP zones can not be ruled out because the observed habit is consistent with the semi-coherent plates frequently observed on Al{111} planes in quenched and aged Al-Si alloys(5). The GP zones revealed in Fig.3 may represent the very early stage of the Si precipitation on Al{111}. It is, however, doubtful that the GP zones are formed during deposition because internally twinned large Si nodules have already been formed in the as-deposited films as shown in Fig.1. The GP zones may, however, be formed during TEM sample preparation when the specimens were heated to 150 °C for 3 min. The latter treatment is sufficient for Si precipiatation to occur in a quenched and aged Al-Si alloy(5).

Figure 1. Planar TEM image shows a twinned silicon precipitate at aluminum grain boundary (A).

The {111} habit of the GP zones is very unfavorable for identifying them as Cu precipiatation. GP zones in Al-Cu alloys have never been observed on Al{111}, the habit plane is always Al {100}(3). However, the following plausible argument can be derived based on the theory of Khachaturyan(15) and Mura(16) to show that GP zones on Al(111) may still be possible to result from Cu precipitation:

The shape and orientation of a coherent inclusion in an isotropic crystal can be determined from analysis of the strain energy. Considering the case of a single coherent cubic phase inclusion in an infinite cubic parent phase matrix, as with the GP zones in Al matrix. Under the assumptions of (1) the dimension of the inclusions and the distance between the nearest inclusions are small compared with the dimension of the crystal (infinite isotropic matrix approximation), (2) external boundaries of the matrix and inclusions mixture are stress free; it has been shown that the habit plane of the inclusion is determined by the elastic aniostropic parameter defined as (15)

$$\xi = (C_{11}\_\, C_{12}\_2\, C_{44})/C_{44}$$

where C_{ij}'s are the elastic constants of the matrix. For $\xi < 0$ the habit plane will be {100} type and for $\xi > 0$ the habit plane will be {111} type. In the case of GP zone in Al-Cu alloy the three non-zero elastic constants of Al are:

$$C_{11} = 10.82 \times 10^{10}\,Pa,\quad C_{12} = 6.13 \times 10^{10}\,Pa,\quad C_{44} = 2.85 \times 10^{10}\,Pa$$

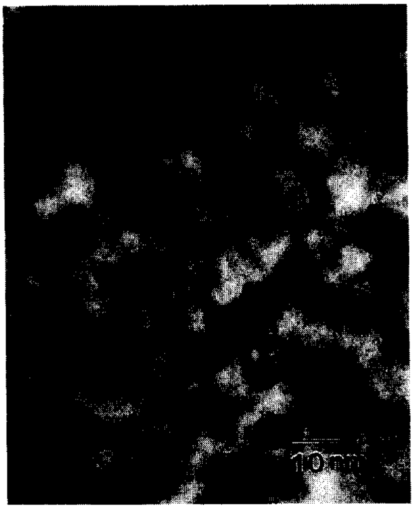

Figure 2. Planar TEM image within an aluminum grain shows parallel dark plates.

and therefore $\xi = -0.365$; thus GP zones should have {100} habit, in agreement with all the experimental obervations made in bulk materials. The situation is different, however, in the case of thin film because the assumptions of the theory may not be satisfied. Of the assumptions mentioned above, the last one is probably most seriously violated because thin metal films on Si substrates are well known to be under external stresses due to thermal incompatibility(17). The validity of the second assumption is certainly less adequate for thin films than for bulk materials. For film thickness of 300 nm and diameter of GP zones about 5 to 10 nm as in the present study, the infinite matrix assumption is also not unquestionable. Although further development of the current theory to the case of stressed thin films is required to explain the observed {111} habit, this possibility is certainly not totally unfounded.

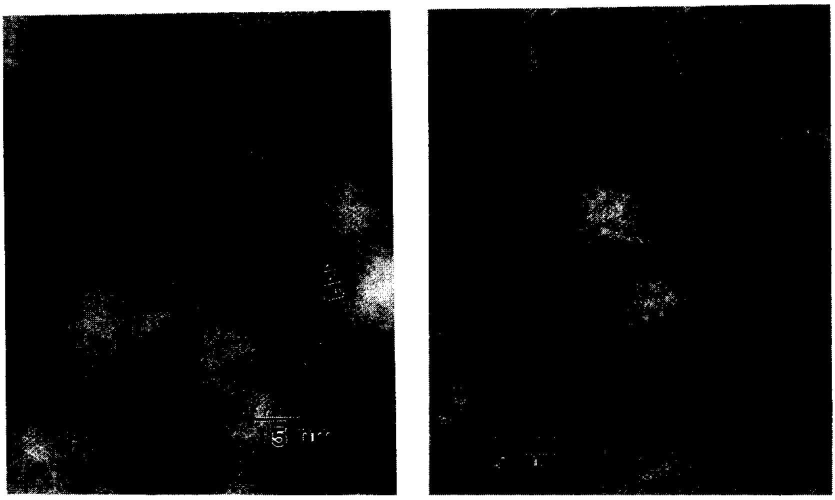

Figure 3. High resolution TEM image shows coherent dark plates along Al {111} lattice planes.

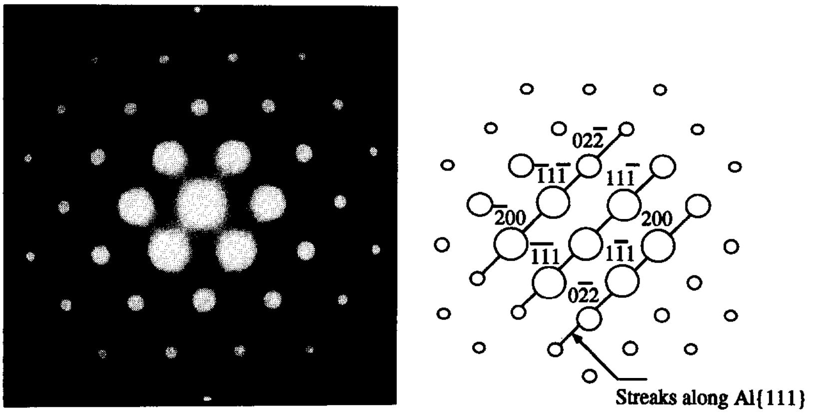

Figure 4. A diffraction pattern from the area shown in Fig. 3. Streaks along <111> are resolved as indicated.

Conclusions

For the first time GP zones are observed by HRTEM to form on Al{111} planes in an as-deposited Al-1wt%Si-0.5wt%Cu thin films sputtered on oxidized Si substrate. At present time the chemical nature (Si or Cu) of the precipitation in the observed GP zones is still uncertain.

Acknowledgment

This work was supported in part by National Science Council of the Republic of China, contract number: NSC 84-00404-E-009-016.

References

1. M.J. Starink, P. van Mourik, Materials Science and Engineering, A156, 183 (1992).
2. M.J. Starink, P. van Mourik, Metall. Trans. 22A, 665 (1991).
3. J.B. Cohen, Solid State Physics, Vol.39, Advances in Research and Applications, edited by H. Ehrenreich, and D. Turnbull, p.131, Academic Press, New York (1986).
4. G.W. Lorimer, Precipitation Processes in Solids, edited by K.C. Russell and H.I. Aaronson, p.87, The Metallurgical Society of AIME, Warrendale, PA (1978).
5. K.H. Westmacott and U. Dahmen, Proceedings of International Symposium on *Behavior of Lattice Imperfections in Materials-In Situ Experiments with High Voltage Electron Microscopes*, p.137, Osaka University, Japan (1985).
6. A. Saulnier, *Mem. Sci. Rev. Metall.* 58, 615 (1961).
7. M. Park, S.J. Krause, and S.R. Wilson, *Appl. Phys. Lett.* 64, 721 (1994).
8. E.G. Colgan, and K.P. Rodbell, *J. of Appl. Phys.* 75, 3423 (1994).
9. C. Kim, and J.W. Morris, Jr., *J. of Appl. Phys.* 72, 1837 (1992).
10. M. Park, S.J. Krause, and S.R. Wilson, *Mat. Res. Soc. Symp. Proc.*, Vol. 229, 313 (1991).
11. D.R. Frear, J.E. Sanchez, A.D. Romig, Jr., and J.W. Morris, Jr., Metall. Trans, 21A, 2449 (1990).
12. R. Venkatraman, J.C. Bravman, W.D. Nix, P.W. Davis, P.A. Flinn, and D.B. Fraser, *J. of Elec. Mater*, 1231 (1990).
13. R.B. Marcus, and T.T. Sheng, *Transmission Electron Microscopy of Silicon VLSI Circuits and Structures*, p.19, Wiley--International, New York (1983).
14. V.A. Phillips, and L.E. Tanner, *Acta. Met.* 21, 441 (1973).
15. A.G. Khachaturyan, *Theory of Structural Transformations in Solids*, p.213, John Wiley & Sons, New York (1983).
16. T. Mura, *Micromechanics of Defects in Solids*, p.815, Martinus Nijhaff Publishers, Netherlands (1982).
17. M.A. Korhonen, P. Borgesen, K.N. Tu, C.-Y. Li, *J. Appl. Phys.* 73, 3790 (1993).