

## Solid-Phase Reactions in Al Alloy/TiN/Ti/Si Systems Observed by In-Situ Cross-Sectional TEM

S. Sobue, S. Mukainakano, Y. Ueno and T. Hattori  
Research Laboratories, Nippondenso Co. Ltd.,  
500-1, Minamiyama, Komenoki, Nisshin-cho, Aichi 470-01, Japan

The mechanism of solid-phase reactions for multilayers of Al-1%Si-0.5%Cu/TiN/Ti/n<sup>+</sup>-Si substrates has been investigated by means of *in-situ* and high resolution/analytical cross-sectional transmission electron microscopy (X-TEM). We observed that an intermediate Al-Ti-Si(-N) layer (~4 nm in thickness) composed of microcrystallites and developed crystallites, began to form at the Al/TiN interface at ~450°C and grew along the TiN grain boundaries. Over ~500 °C, the Al immediately diffused downward through the TiN layer, forming an Al region under the TiN layer. It has been concluded that the rapid redistribution of the Al may be caused by movement in the microcrystalline phases preferentially.

### 1. INTRODUCTION

Titanium nitride (TiN) has attractive properties and characteristics of both covalent compounds such as high melting points and thermodynamic stability, and of metals such as good thermal and electrical conductivities. For microelectronics applications, TiN is used as a diffusion barrier material between a Si substrate and an interconnecting metal, (i.e., Al alloy), in integrated circuits<sup>1</sup>). However, the diffusion barrier properties with reactively sputtered TiN films are not thermally stable in contact with Al alloy/TiN/Ti/Si systems<sup>2-5</sup>) because the chemical and crystallographic characteristics of the reactive-sputtered TiN are sensitive to the deposition condition of the TiN films. In order to improve the reliability of the TiN diffusion barrier, it is necessary to sufficiently clarify the mechanism of the barrier breakdown of the TiN films. In this study we carried out a real-time observation of the reaction process in Al-1%Si-0.5%Cu/TiN/Ti/Si systems by means of *in-situ* cross-sectional transmission electron microscopy (X-TEM) and investigated precisely the chemical and crystallographic state of the Al alloy/TiN interface around temperatures of the barrier breakdown by means of high resolution (HR) / analytical X-TEM. The present work seeks to elucidate the mechanisms of a breakdown of reactive-sputtered TiN barrier properties.

### 2. EXPERIMENTAL PROCEDURE

Samples used were multilayers of Al-1%Si-0.5%Cu/TiN/Ti/n<sup>+</sup>-Si to study the solid-phase reaction mechanism. The n<sup>+</sup>-type Si (100) substrates were implanted with phosphor at 150 keV with doses of  $1.0 \times 10^{15}$  /cm<sup>2</sup> and were chemically cleaned by dipping in a diluted HF solution just before loading into a deposition chamber. The base pressure of the

chamber was better than  $5 \times 10^{-7}$  Torr. The Ti films of 20 nm thickness were deposited onto the Si substrates by r.f. sputtering. Sequentially 80 nm of the TiN films were deposited by reactive sputtering and finally Al alloy films were deposited by r.f. sputtering. Owing to the continuous deposition without air explosion, no oxygen existed both in each film and at each interface. The temperature of the substrates was 230 °C during deposition. The specimens for *in-situ* X-TEM observation were prepared by Focused-Ion-Beam (FIB) technique<sup>6,7</sup>) (Fig. 1) and were annealed in a heatable sample stage equipped with a TEM device up to ~600 °C. The annealing temperature of the specimens was monitored with an Pt-PtRh(13%) thermocouple connecting to the heatable sample holder and rose at a rate of ~2 °C/min and was maintained for 5 min at each temperature from 200 °C to 600 °C per increase of 50 °C. The *in-situ* TEM observation, using a JEM-200CX

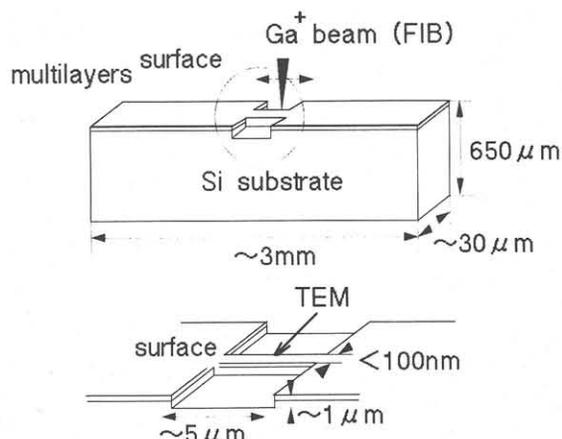


Fig.1 Draws of *in-situ* X-TEM specimens prepared by FIB technique.

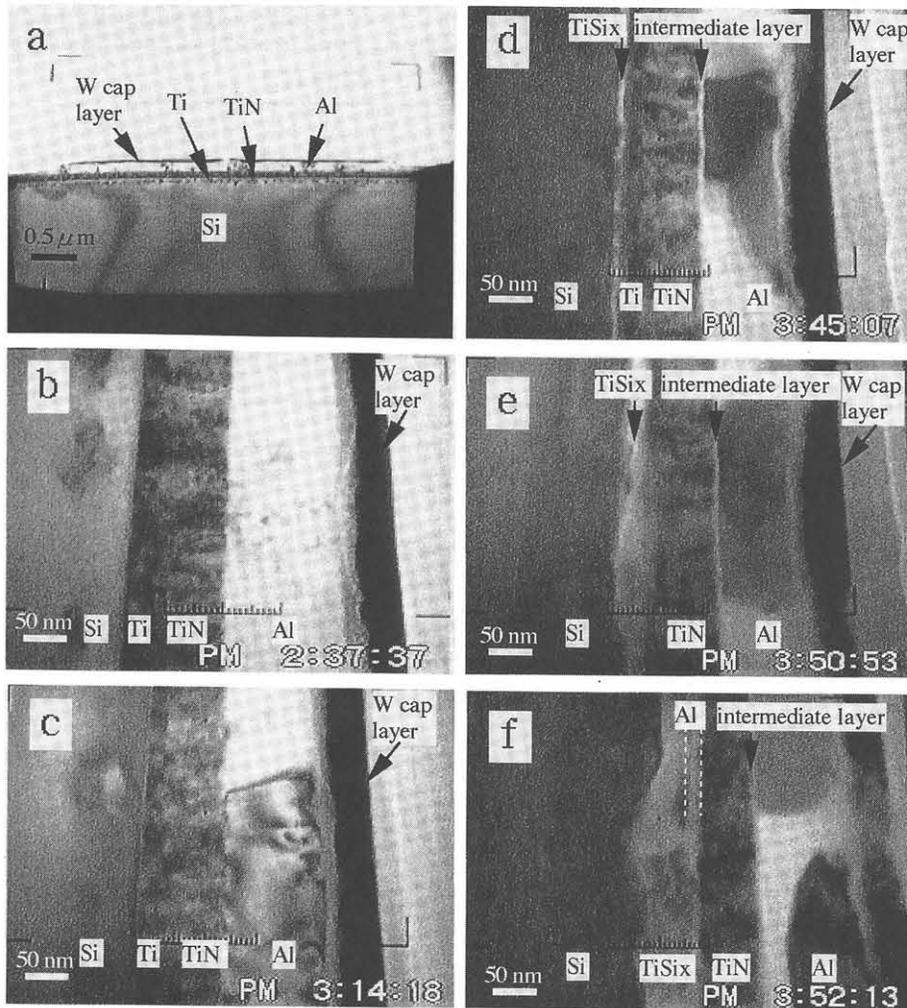


Fig. 2 *In-situ* X-TEM images, observed by a CCD camera, for the samples (a,b) before and during annealing at the temperature of (c)  $\sim 300$  °C, (d)  $\sim 450$  °C, (e)  $\sim 508$  °C and (f)  $\sim 514$  °C, respectively.

TEM device, was carried out by monitoring/recording the fluorescent screen reflecting the reactions with a CCD video camera. The other samples for HR/analytical X-TEM were annealed in the furnace with  $N_2$  and  $H_2$  ambient at 450 °C and 550 °C, respectively. The HR/analytical TEM device used was JEM-2010F field emission electron microscope with a line resolution of 0.1 nm, equipped with an energy dispersive X-ray spectrometer (EDS), the specimens for which were prepared by conventional ion milling technique.

### 3. RESULTS AND DISCUSSION

#### 3.1 *In-situ* X-TEM

Figure 2a shows a low magnified X-TEM image of a specimen prepared by using a focused  $Ga^{+}$ -ion beam. Since the thinned part of the multilayer is supported by the Si bulk, the thermal drift of the specimen during heat procedure kept very low as to allow stable *in-situ* X-TEM observation. By *in-situ* X-TEM observations using this specimen, we made clear how the breakdown of the TiN diffusion barrier proceeds. Figure 2b shows a magnified X-TEM image of a sample before annealing, which indicates

that the TiN layer was composed of densely packed columnar crystals of TiN. The diameter and the length of the TiN grains were about 20 nm and about 80 nm, respectively. When the annealing temperature was increased to  $\sim 300$  °C, the Al grains got larger and larger but no changes happened both at the Al alloy/TiN interface and at the Ti/Si interface (Fig. 2c). At  $\sim 450$  °C, an intermediate layer (about 4 nm in thickness) began to be formed at the Al alloy/TiN interface (Fig. 2d). At the same time, a Ti silicide layer was formed at the Ti/Si interface (Fig. 2d) and gradually grew out (Fig. 2e). The crystalline structure of the TiN seemed to be almost maintained. Elevated over  $\sim 500$  °C, however, the contrast among the columnar grains of the TiN became blurred slightly and then the Al immediately diffused downward through the TiN layer, at least for less than a few minutes, forming an Al region under the TiN layer (Fig. 2f). The changes were too rapid to observe the initial breakdown positions in the TiN layer during annealing over  $\sim 500$  °C. In order to understand the mechanism of the rapid redistribution of Al, it is necessary to investigate microscopic changes at the Al alloy/TiN interface just before and during barrier

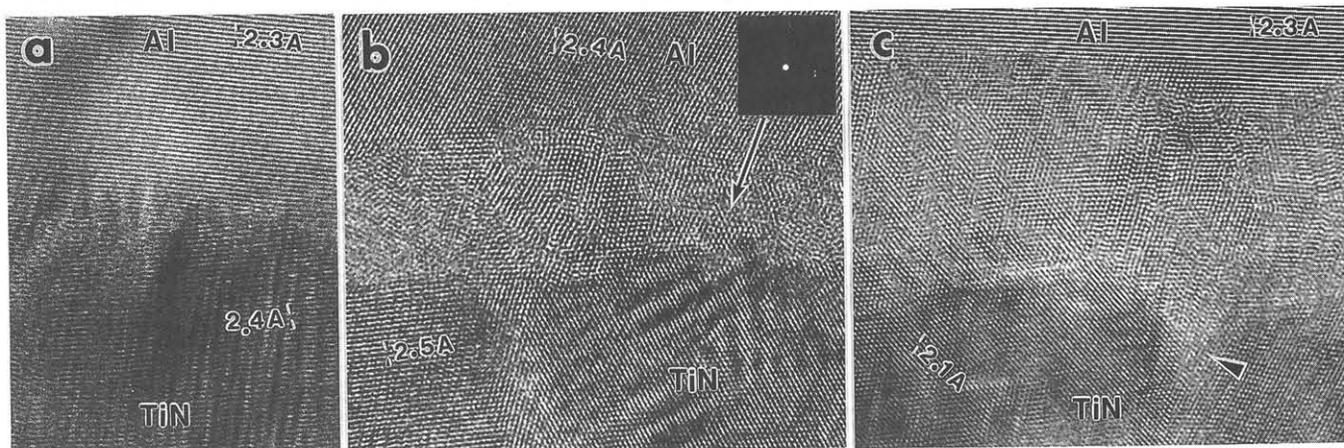


Fig. 3 High resolution X-TEM images of the Al alloy/TiN interfaces (a) before and after annealing at (b)  $\sim 450^\circ\text{C}$  and (c)  $550^\circ\text{C}$  for 30 min, respectively. The incident electron beam is in  $[011]_{\text{Al}}$ .

breakdown. The HR/analytical X-TEM observation provided effective information for this purpose.

### 3.2 High Resolution / Analytical X-TEM

Figure 3 shows lattice images of the Al alloy/TiN interface of the samples before and after annealing at  $450^\circ\text{C}$  and  $550^\circ\text{C}$  for 30 min, respectively. The Al alloy/TiN interface before annealing was relatively sharp but after annealing at  $450^\circ\text{C}$  an intermediate layer presenting short-ranged lattice fringes, in addition to long-ranged lattice fringes, formed there in a continuous layer. By means of electron diffraction (ED) and EDS analysis using an electron beam 0.7 nm in diameter, the microcrystalline and chemical state of the intermediate layer was determined. The ED pattern from this layer was comprised of diffraction spots in the very weak ring, which indicates a microcrystalline state like amorphous state. According to the EDS analysis, it contains 73 at% Al, 15 at% Ti, 10 at% Si and 2 at% Cu (except light element such as C, N and O). Although this layer was also analyzed by conventional Auger depth profiling to confirm an existence of oxygen contamination, no oxygen signal was detected<sup>8)</sup>. It is thought that the reaction between the Al and TiN at the Al-Si-Cu/TiN interface thermodynamically takes place following the reaction:



As the difference between the value of the standard heat of formation before and after the reaction of (1),  $\Delta H_{298}$ , is  $-4.95 \text{ kcal/g} \cdot \text{atom}$ , the reaction of (1) can thermodynamically occur. Furthermore, it is noteworthy that the Si in the Al alloy segregated slightly in this layer. This fact was also confirmed by Auger depth profiling in our previous work<sup>8)</sup>. Kottke et. al have also reported that firstly Ti and Al interdiffuse through the TiN to form  $\text{Al}_3\text{Ti}$  and then the  $\text{Al}_3\text{Ti}$  compounds reacts with Si to form a ternary Al-Ti-Si compound in Al-1% Si-1%Cu/TiNx/TiSix/n<sup>+</sup>-Si systems<sup>1)</sup>. It is said in general that amorphous alloys including minority of metalloid atoms, such as Si, B and P, are transferred to crystalline phases via forming microcrystalline phases (metastable phases), which are in a mobile state<sup>9,10)</sup>. It is considered that the Al diffuse along the paths of the

metastable phase formed by the reaction between the Al and the TiN. As shown in Fig. 3c, the metastable phases are formed not only at the Al alloy/TiN interface but also along the TiN grain boundaries (indicated by the arrow). Therefore it is concluded that the rapid diffusion of the Al around  $\sim 500^\circ\text{C}$  may be caused by movement in the microcrystalline phases preferentially.

### 4. SUMMARY

This mechanism of solid-phase reactions for multilayers of Al-1%Si-0.5%Cu/TiN/Ti/n<sup>+</sup>-Si substrates has been investigated by means of *in-situ* and high resolution/analytical cross-sectional transmission electron microscopy (X-TEM). We observed that an intermediate Al-Ti-Si(-N) layer ( $\sim 4 \text{ nm}$  in thickness) composed of microcrystallites and developed crystallites, began to form at the Al/TiN interface at  $\sim 450^\circ\text{C}$  and gradually grew along the TiN grain boundaries. Over  $\sim 500^\circ\text{C}$ , immediately the Al diffused downward through the TiN layer, forming an Al region under the TiN layer. It has been concluded that the rapid redistribution of the Al may be caused by movement in the microcrystalline phases preferentially.

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