

# Multilayer diffusion barrier scheme using a thin metal interlayer (M=Al, Ru, Cr, and Zr) between TiN films for Cu metallization

Ki-Bum Kim<sup>a</sup>, Soo-Hyun Kim, Ki Tae Nam<sup>b</sup>, Arindom Datta<sup>c</sup>, Dae-Hwan Kang<sup>d</sup>, and Hyun-Mi Kim

*School of Materials Science & Engineering,  
Seoul National University, Seoul 151-742, Korea  
Research Institute of Advanced Materials<sup>d</sup>  
Seoul National University, Seoul 151-742, Korea*

<sup>b</sup>*Present address: Materials Science and Engineering, MIT, USA*

<sup>c</sup>*Present address: Department of Physics, Texas Tech. University, USA*

<sup>a</sup>Author to whom correspondence should be addressed; E-mail: [kibum@snu.ac.kr](mailto:kibum@snu.ac.kr)

## 1. Introduction

The transition to copper metallization, from aluminum-based metallization, for sub-quarter-micron advanced devices has posed many challenges. One of the challenges is to find a suitable diffusion barrier for preventing the unavoidable reaction between the top metallization layer and the underlying substrate, such as Si or SiO<sub>2</sub> and potentially low-*k* materials. One of the best choices for a diffusion barrier material is titanium nitride (TiN) because of its current use in Al metallization. Therefore, the process technology for this material is well developed. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes allow one to obtain TiN films with good step coverage and low resistivity. In addition, its columnar grain structure, providing a fast diffusion path for an overlying metal, can be tailored by a stuffing mechanism, leading to good barrier performance [1]. However, this kind of stuffing mechanism, which works well for Al-based interconnect, would not be expected for Cu because the reaction of the Cu with oxygen is thermodynamically less favorable [2]. These shortcomings of TiN films as a diffusion barrier for Cu are more problematic with decreasing its thickness, because of the columnar microstructure.

## 2. Experiments

A multilayer diffusion barrier deposited by sputtering [TiN(5nm)/Al/TiN(5nm)] for Cu metallization, using Al as a stuffing material by its reaction with oxygen in TiN film has been developed [3]. In this scheme, the intended final structure is composed of two different barrier materials; one is the parent barrier layer (TiN in our case) and another one locates along the grain boundaries of the parent barrier layer (Al<sub>2</sub>O<sub>3</sub> in our case). Other metals such as Ru, Cr, and Zr are also evaluated as interlayer materials. The barrier performances of multilayer structures have been evaluated using etch-pit test, sheet resistance measurement, cross-sectional transmission electron microscopy (XTEM), and x-ray diffractometry (XRD).

## 3. Results and Discussion

It has been shown, according to etch-pit test, the failure temperature for the multilayer barrier structure [TiN(5nm)/Al(2nm)/TiN(5nm)] was 700°C, i.e., 250°C higher than that of the TiN (10nm) without an Al interlayer. Our results show that the well-developed materials, TiN and Al, can be used as diffusion barrier materials for Cu metallization, which can give a technological and economical advantage [3]. The barrier performance is enhanced proportionally with increasing Al thickness (from 0.5 nm to 2 nm) in case of preannealed upper TiN, showing the best result for 2 nm thick Al interlayer

[Fig. 1(a)] [4]. On the other hand, in not preannealed upper TiN, barrier property is at its best when Al thickness is 1 nm, but above this value, the barrier performance becomes very poor [Fig. 1(b)].

We have also investigated the reason why the barrier breaks down at above 1 nm of Al interlayer thickness and corresponding failure mechanism of the present diffusion barrier scheme [5]. High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS) analyses reveals that the fast diffusion of Cu in the presence of the free Al is the main reason for the failure of the present diffusion barrier scheme (Fig. 2). These results are discussed on the basis of the differences between the movements of Al and Cu through TiN film, and the differences between the solid solubilities of Al in Cu and in Si. Our results show that both Al interlayer thickness and the oxygen content in TiN film should be properly controlled to take full advantage of the present multilayer diffusion barrier scheme.

Finally, the effect of other interlayer materials (M=Ru, Cr, and Zr) on the diffusion barrier performance of TiN film has been investigated [6]. Diffusion barrier performance is shown to be the best when the Zr was used as an interlayer material [Fig. 3]. The sheet resistance of Zr-interlayered diffusion barrier [TiN(5nm)/Zr(2nm)/TiN(5nm)] did not increase with respect to as-deposited value until 800°C (Fig. 3). The insertion of Cr also improved the diffusion barrier performance while the insertion of Ru did little the barrier property of TiN film. An explanation of the variation of diffusion barrier performance with the change of interlayer metal is given in terms of Gibbs free energy change ( $\Delta G$ ) of the respective metal oxide formation.

#### 4. Conclusions

Multilayer structures [TiN(5nm)/interlayer metal (Al, Ru, Cr, and Zr, 2nm)/TiN(5nm)] have been evaluated as diffusion barriers between copper and silicon. Improved diffusion barrier performance of the multilayer structure is probably due to the formation of metal oxide in the TiN grain boundaries, which is critically dependant on the  $\Delta G$  of the respective metal oxide formation. However, the thickness of metal interlayer and oxygen content in the TiN film should be properly controlled in order to take full advantage of the present multilayer diffusion barrier scheme. Our results show that the multilayer structure is a viable candidate of a diffusion barrier for Cu metalliation that satisfies mane of requirements for diffusion barrier layer down to a 0.1  $\mu\text{m}$  device.

#### References

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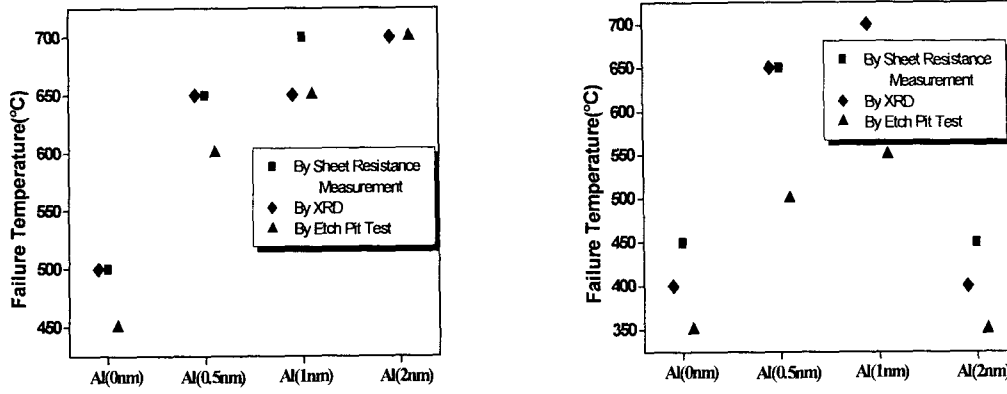


Figure 1. (a) Summary of failure temperatures as characterized by sheet resistance measurements, XRD, and secco etching in case of preannealed upper TiN and (b) upper TiN not preannealed.

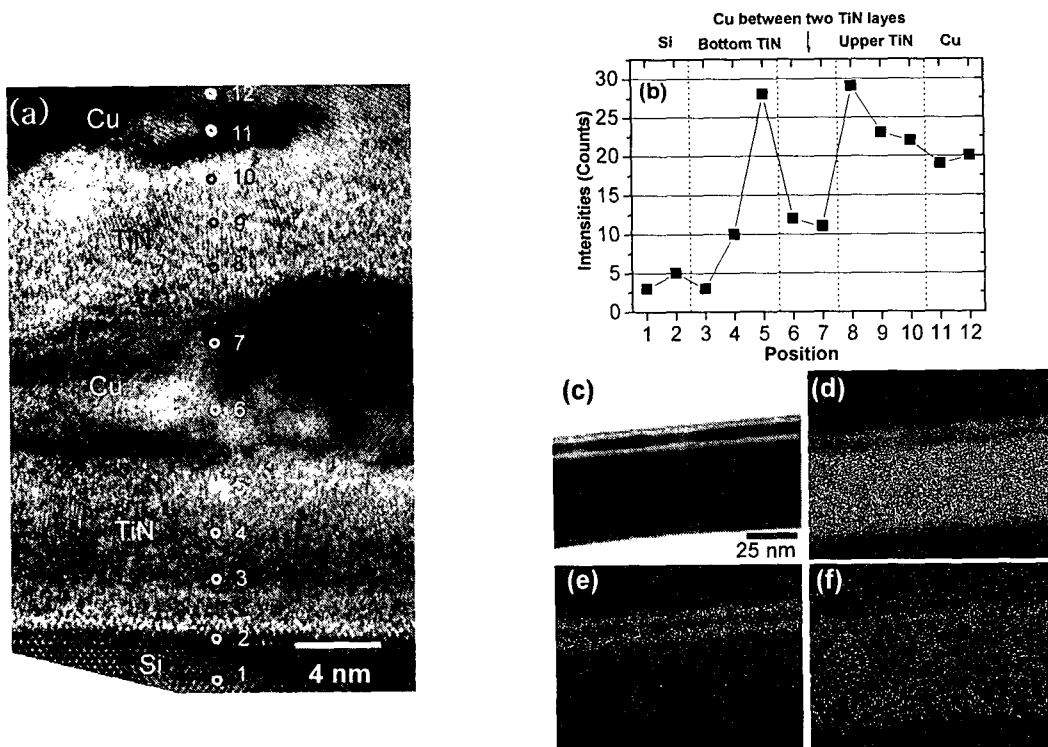


Figure 2. (a) High resolution TEM images of the sample annealed at 550 °C, and (b) the variation of x-ray intensities of Al K $\alpha$  line from Si to Cu. Positions, where the EDS data were taken, were shown in (a), (c) STEM image of the sample annealed at 550 °C, (d) corresponding STEM-EDS mapping data for Cu, (e) Ti, and (f) Al.

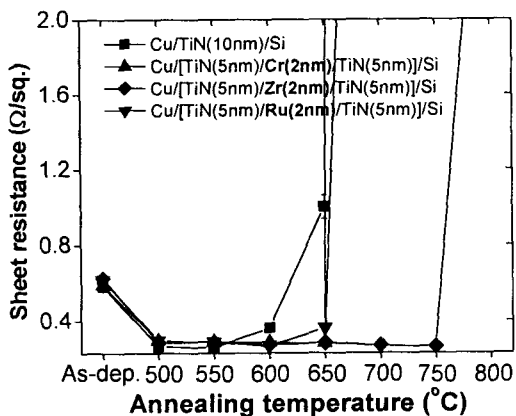


Figure 3. Sheet resistance changes of Cu/TiN(~10nm)/Si, Cu/TiN(5nm)/Ru(2nm)/TiN(5nm)/Si, Cu/TiN(5nm)/Cr(2nm)/TiN(5nm)/Si, and Cu/TiN(5nm)/Zr(2nm)/TiN(5nm)/Si samples as a function of annealing temperature.