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Copper Thermal Diffusion in TaN Film on Si Substrate

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Thermal diffusion of copper in a Cu/TaN/Si-sub sample was investigated after annealing at 630°C for 60 min. The interface morphology, copper silicide grains and SiO₂ thin layer were observed using high resolution transmission electron microscope (HRTEM). Depth profiles were obtained with an energy dispersion X-ray spectrometer (EDS) assembled in the TEM system. Based on the grain boundary theory of Fisher and the approximation solution of Le Claire, thermal diffusivity of copper into the tantalum nitride layer was estimated. [DOI: 10.1143/JJAP.41.6525]

KEYWORDS: barrier layer, grain boundary diffusion, Cu interconnection, transmission electron microscopy, interface

1. Introduction

With the development of deep submicron integrated circuits (ICs), copper metallization has been a substitute for conventional aluminum metallization in the manufacture of high-density IC.¹⁾ Copper has superior resistance against electromigration, low electrical resistivity, low power dissipation and short RC delay, but it is quite mobile in Si, which could induce very high leakage current or a short circuit.²⁾ Therefore, it is necessary to deposit a diffusion barrier layer between the copper interconnection and the Si device.

Some metal nitrides, oxides and silicides have been known to be effective barrier layers for copper interconnection, such as Ti–N, Ta–N, Ta–Si–N, W–N and Ta–O. Among these compounds, TaN is very attractive due to its high thermal stability, good adhesion, high melting point and low resistivity (25–250 $\mu\Omega/\text{cm}$).³⁾ Thermal diffusion and reactions within the barrier layer, copper layer and Si device are important for the reliability of copper metallization. In this study, the depth profile was attained by energy dispersion X-ray spectrometer (EDS) in combination with transmission electron microscope (TEM) observation of Cu/TaN/Si-sub samples. The thermal diffusion coefficient of copper in TaN film annealed at high temperature was estimated.

2. Experimental

A tantalum nitride layer was deposited onto a clean Si substrate by rf magnetron sputtering of the Ta target with sputtering gases of N₂ and Ar. The flow ratio of N₂/Ar was 0.3 while the flow rate of Ar was maintained at 8 sccm. The bias voltage of the substrate was 0 V, the deposition pressure was 1×10^{-2} Torr and the rf power was 300 W. The thickness of TaN_x was 100 nm, in which $x = 1.06$ was determined from the peak area normalized with the respective relative sensitivity factor of each component in the photo electron spectroscopy (XPS) spectrum. Then an 80-nm-thick Cu layer was deposited *in situ* on TaN/Si by chemical vapor deposition (CVD) using (hfac)Cu^I (1,5-COD) as the precursor. During CVD, the deposition temperature was 180°C and the N₂ flow rate was 10 sccm/min. This multilayer sample was annealed in N₂ atmosphere at 630°C for 60 min. In order to observe the diffusion

phenomena of copper into the TaN layer, we selected a thick barrier layer and high annealing temperature.

Interfaces of Cu/TaN/Si-sub samples were analyzed by TEM (Philips, CM200FEG). The experimental high tension was 160 kV. High resolution transmission electron microscope (HRTEM) and diffraction were also performed to observe the crystal images and analyze the crystal structure. Depth profiles of Cu, Ta and Si were measured with EDS which is assembled in the TEM system. The diameter of the electron beam for EDS measurement was 3.5 nm. RBS of 2 MeV ⁴He²⁺ ions was used to analyze the thickness and depth profiles of multilayer samples before and after annealing.

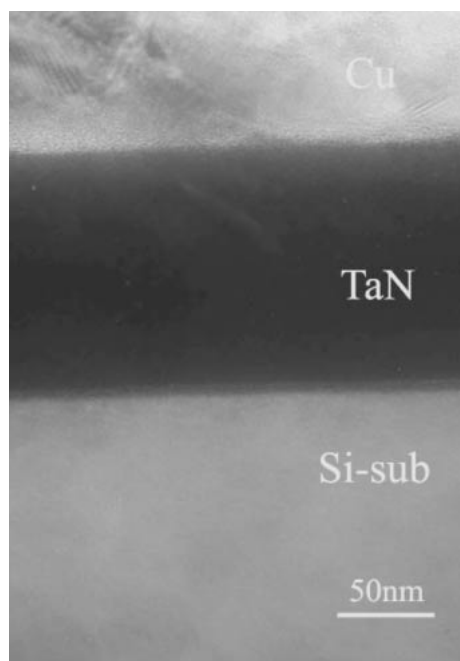
3. Results and Discussion

3.1 TEM observation

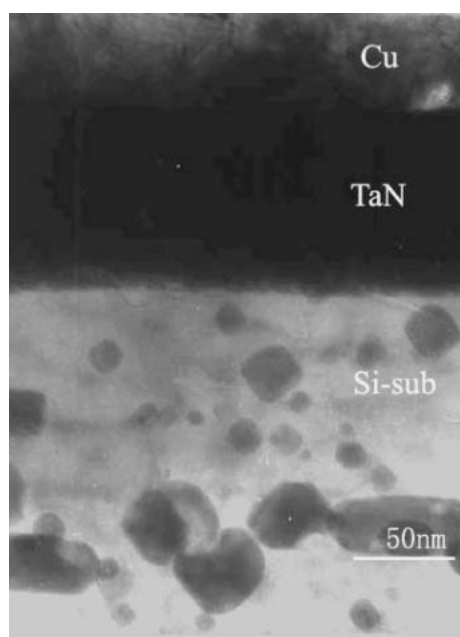
Figures 1(a) and 1(b) show the TEM images of the Cu/TaN/Si-sub sample before and after annealing. The TaN/Si-sub interface of the annealed sample remains as flat as that of the original sample. In Fig. 1(b), there are some dark grains near the interface in the Si layer. In Fig. 2, EDS measurement indicates that they are composed of Cu and Si. Figure 3 shows the HRTEM image of a Cu–Si grain that is a result of the reaction between the diffused copper and the Si layer.⁴⁾ This means that after annealing at 630°C for 60 min, the copper diffuses into the Si substrate through the TaN barrier layer. Copper is the mobile element in the thermal reaction of Cu and Si. During the movement of copper, the Si–Si bond is broken, and then the reaction takes place even below 200°C. Some copper silicides may be formed. For example, Cu₃Si is a rather stable compound and easily forms when Cu reacts with bulk Si.⁵⁾

Figure 4 shows the HRTEM image of a deeply buried amorphous layer near the interface of TaN/Si-sub. EDS measurement indicates that it is a SiO₂ layer with a thickness of about 25–30 Å. The thickness of this SiO₂ layer increased after one-week storage. Generally, thermal oxidation of Si takes place above 700°C, but it can occur at room temperature if catalyzed by a Cu–Si compound.⁶⁾ The reaction of copper silicides with O results in Cu and SiO₂. These Cu atoms diffuse deeper into the Si substrate and then react with Si atoms to form new Cu silicides, thus these reactions go cycle. Oxygen in the above reactions mainly comes from the penetration of air through the surface Cu layer and the TaN layer. After a thick SiO₂ layer is formed, it is difficult for oxygen to diffuse deeper into the Si layer

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(a)



(b)

Fig. 1. TEM images of the interface of the Cu/TaN/Si-sub sample (a) before and (b) after annealing.

and then the reactions almost stop. If oxygen can continuously diffuse deeper into the Si substrate, the thickness of the SiO₂ layer will increase subsequently.

3.2 Analysis of depth profile

Starting at the interface of Cu/TaN, we set 16 equidistant points along the line that is perpendicular to the surface to perform EDS analysis of the Cu/TaN/Si-sub samples, respectively. Figures 5(a) and 5(b) show the depth profiles of Cu, Ta and Si before and after annealing. (Signals of N are too weak to be clearly identified from the EDS

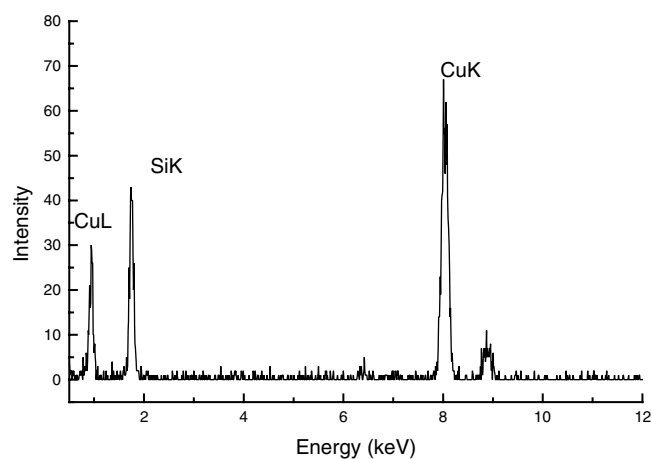


Fig. 2. EDS spectrum of copper silicide grain.

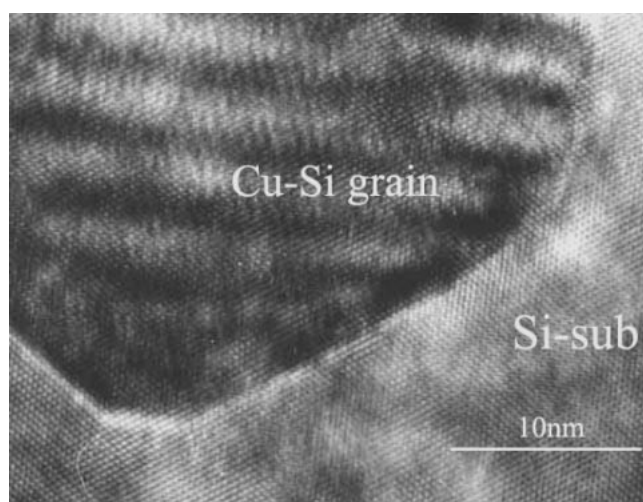


Fig. 3. HRTEM image of copper silicide grain.

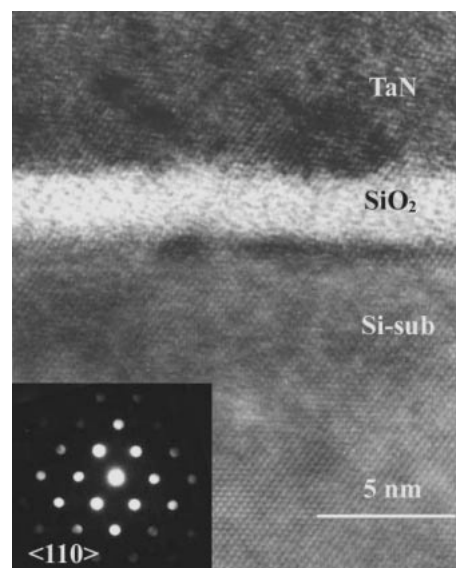


Fig. 4. HRTEM image of buried SiO₂ layer.

background noise.) In Fig. 5(a), copper is totally in the surface layer before annealing. In Fig. 5(b), outside of the copper surface layer, there is a peak of copper signals

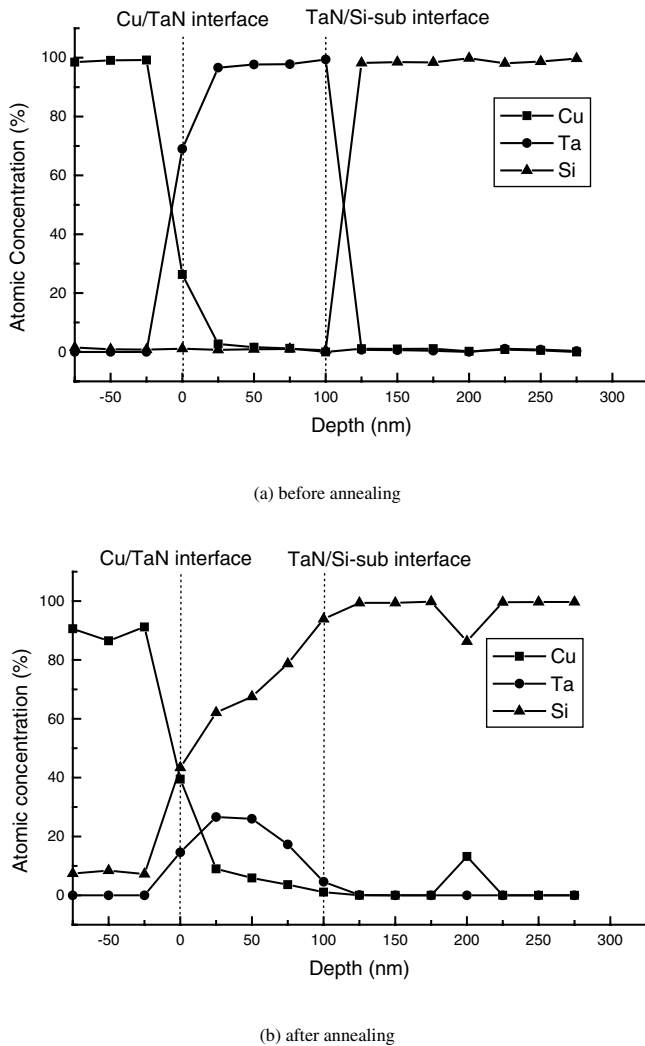


Fig. 5. Depth profiles of Cu, Ta and Si in samples (a) before and (b) after annealing.

200 nm away from the interface of TaN/Si-sub, corresponding to the region of copper silicide grains shown in Fig. 1(b). This Cu peak results from a Cu–Si grain lying on the line set for EDS analysis. Meanwhile, Si signals in the TaN layer are intensified as shown in Fig. 5(b). For the TaN barrier layer, extra energy is necessary to break the bond between Ta and N to form tantalum silicides, while the Cu/Ta/Si-sub multilayer sample can easily form TaSi_2 .⁷⁾ It was reported⁸⁾ that TaN_x can be partly decomposed into some bcc Ta at 500–600°C and these Ta atoms react with Si to form tantalum silicide. Additionally, the mobile Si atoms in the reaction of Ta and Si can more easily move when Cu silicide breaks the Si–Si bond. Thereby the silicidation of Ta is promoted.

As a complement, RBS is used to determine element concentrations of the samples before and after annealing. Figure 6 shows that the back edge, namely the low-energy edge of the copper peak, stretches backwards apparently after annealing. This means that the copper layer has diffused towards the underlying TaN layer and Si substrate. The front edge, namely the high-energy edge of the Ta peak, moves slightly forward. This results from copper thermal diffusion and the movement of Ta atoms to the Cu layer. The back edge of the Ta peak also extends backwards, which

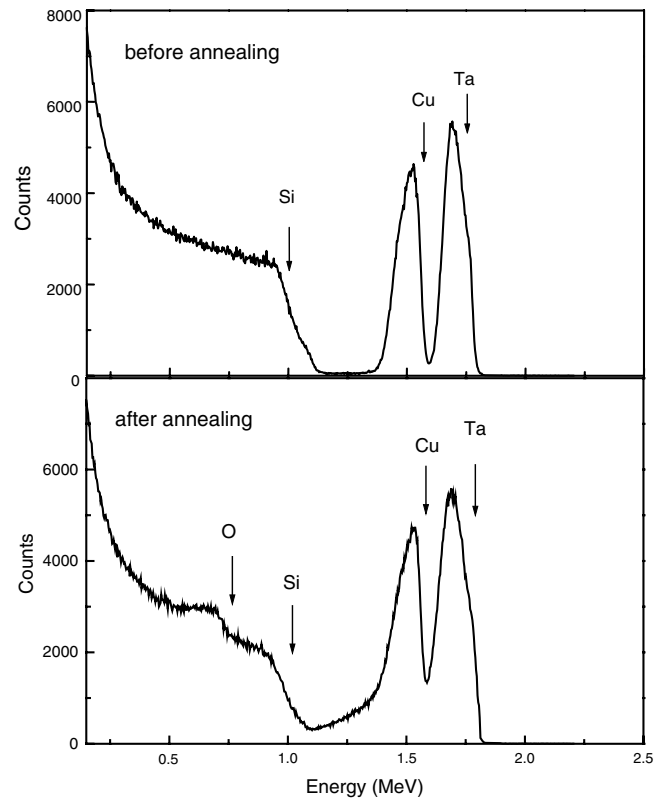


Fig. 6. RBS spectrum of Cu/TaN/Si-sub samples before and after annealing.

means that Ta in the TaN layer moves to the Si substrate after annealing at high temperature. At the same time, from the change of slopes of the front edges of Si spectra in Fig. 6, it can be found that the concentration of Si near TaN/Si decreased after annealing. This is due to the formation of copper silicide and Ta silicide which consume some of the Si atoms.⁹⁾ These phenomena agree with TEM observation quite well.

3.3 Estimation of thermal diffusion coefficient of copper in TaN layer

In Fig. 7, the TaN layer deposited by rf magnetron sputtering shows a polycrystalline structure with a grain size of 10–20 nm. Grain boundaries exist between the grains with different crystal directions. In the range of 600–800°C, the activation energy of grain boundary diffusion is only one-half that of lattice diffusion. When the temperature is higher than $0.3T_m$ (800°C), lattice diffusion is important.³⁾ Therefore grain boundary diffusion of copper dominates in polycrystalline TaN film in our experiment. The main mechanism of grain boundary diffusion in bulk materials is B-type dynamics.¹⁰⁾

It is assumed that a fixed concentration of diffusing materials is maintained on the surface, with a zero initial concentration in the bulk. The grain boundary is a semi-infinite thin slab of high-diffusivity material imbedded in semi-infinite solid. The concentration of diffusing material in the grain boundary, denoted by C_b , is a function of depth y only. The x -axis is parallel to the surface. The variation of C_b is so slow during the proceeding diffusion that $\partial C_b / \partial t$ can be assumed to be 0, where t is diffusion time. According to the solution given by Fisher, an approximate expression for

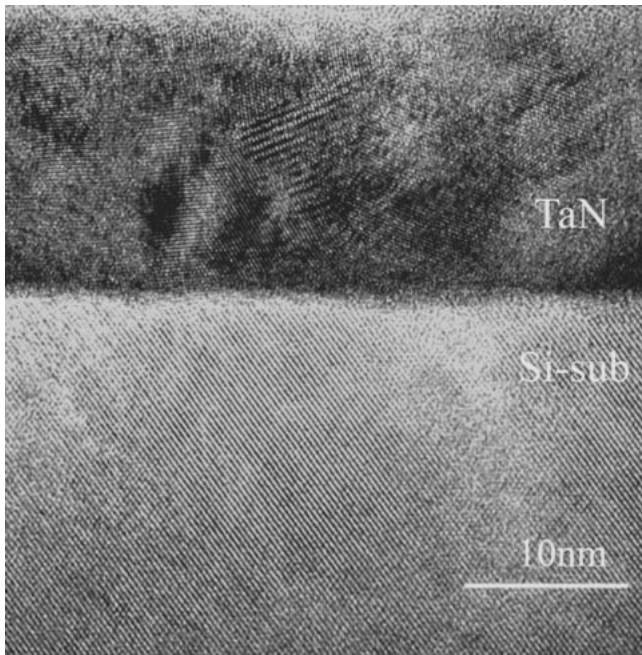


Fig. 7. HRTEM image of polycrystalline TaN films as-deposited.

grain boundary diffusion¹¹⁾ is represented as

$$C = \exp(-2^{\frac{1}{2}}y_1/\pi^{\frac{1}{4}}t_1^{\frac{1}{4}}) \operatorname{erfc}(x_1/2t_1^{\frac{1}{2}}), \quad (1)$$

where C is the concentration of diffusing material and

$$\begin{aligned} t_1 &= Dt/\delta^2 \\ x_1 &= x/\delta \\ y_1 &= y/[\delta(D'/D)^{1/2}], \end{aligned} \quad (2)$$

δ is the width of the grain boundary, and D' and D are diffusion coefficients inside and outside the grain boundaries, respectively.

Le Claire simplified the Whipple solution¹²⁾ based on eq. (1), and obtained

$$D_b\delta = 0.661 \left(-\frac{\partial \ln C}{\partial y^{6/5}} \right)^{-5/3} \left(\frac{4D_l}{t} \right)^{1/2}, \quad (3)$$

where D_l and D_b are the grain boundary diffusion coefficient and the lattice diffusion coefficient, respectively. The grain boundary contribution in a plot of $\ln C$ vs $y^{6/5}$ is extremely close to a linear function. Assuming that D_l is known, D_b can be determined from eq. (3) with the slope of the linear region of the curve, and D_l can be determined from the initial part of the curve expressed by

$$C = C_0 \operatorname{erfc} \left[\frac{y}{2(D_l t)^{1/2}} \right], \quad (4)$$

where C_0 denotes an infinite source concentration. In our EDS measurement, due to the limitation of the diameter of the electron beam and the step length of the depth profile measurement, the initial nonlinear part (within about 1 nm) of the $\ln C$ vs $y^{6/5}$ curve cannot be measured directly. We

introduce $D_l = 5.16 \times 10^{-18} \text{ cm}^2/\text{s}$ ¹³⁾ taken from the data obtained under a similar experimental condition at annealing temperature $T = 630^\circ\text{C}$ and $t = 3600 \text{ s}$ for the Cu/TaN_{0.99}/Si-sub sample. It is assumed that $\delta = 5 \times 10^{-8} \text{ cm}$, a thickness of about two atom layers.^{10,11,13)} With the slope of $\ln C$ vs $y^{6/5}$ curve attained from experimental concentration profiles and the introduced D_l , the estimated value of D_b is $1.57 \times 10^{-16} \text{ cm}^2/\text{s}$. The error of D_b resulting from the error of D_l induced by the difference in TaN_x composition is smaller than $1.31 \times 10^{-18} \text{ cm}^2/\text{s}$,¹³⁾ which is 10% of D_b . At this experimental temperature or the actual processing temperature, the lattice diffusion plays only a minor role and the variation of D_l for copper in different TaN_x layers is very small at the temperature range from 400°C to 800°C . Thus it is acceptable to introduce D_l taken from a similar experiment for D_b estimation.¹³⁾

The calculations above are based on the depth profile measured by EDS. EDS is a semi-quantitative method and its data of EDS are not as accurate as that of AES. However EDS measurement is convenient to perform simultaneously as TEM observation and the structural image and element concentration are attained directly. With the slope of $\ln C$ vs $y^{6/5}$ from experimental data, the value of D_b can be calculated. However the value of D_l is difficult to be determined from EDS measurement directly.

4. Conclusion

With the TaN layer deposited by rf sputtering being used as the diffusion barrier of the Cu layer deposited by CVD, the interface morphology, element depth profile and thermal diffusion of annealed Cu/TaN/Si-sub samples were investigated. After annealing at 630°C for 60 min, copper diffused through the polycrystalline TaN barrier layer to the Si substrate. Copper silicide grains and tantalum silicide were formed. A SiO₂ layer was observed at the TaN/Si-sub interface. With $\partial \ln C / \partial y^{6/5}$ attained from EDS measurement, the approximation of thermal diffusivity was calculated with the Le Claire solution.

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