

Copper diffusion in Ti–Si–N layers formed by inductively coupled plasma implantation

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Received 18 March 2005; accepted 15 December 2005

Available online 8 February 2006

Abstract

Ternary Ti–Si–N refractory barrier films of 15 nm thick was prepared by low frequency, high density, inductively coupled plasma implantation of N into Ti_xSi_y substrate. This leads to the formation of Ti–N and Si–N compounds in the ternary film. Diffusion of copper in the barrier layer after annealing treatment at various temperatures was investigated using time-of-flight secondary ion mass spectrometer (ToF-SIMS) depth profiling, X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) and sheet resistance measurement. The current study found that barrier failure did not occur until 650 °C annealing for 30 min. The failure occurs by the diffusion of copper into the Ti–Si–N film to form Cu–Ti and Cu–N compounds. FESEM surface morphology and EDX show that copper compounds were formed on the ridge areas of the Ti–Si–N film. The sheet resistance verifies the diffusion of Cu into the Ti–Si–N film; there is a sudden drop in the resistance with Cu compound formation. This finding provides a simple and effective method of monitoring Cu diffusion in TiN-based diffusion barriers.

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Keywords: TiSiN; Copper diffusion

1. Introduction

When the electronic industries advance into nanoscale feature size, research and development effort on advanced materials and/or alternative process techniques for copper metallization is rapidly increasing. For the next generation of devices, the primary focus is on new materials and their process integration such as low-*k* dielectric, copper and barrier materials. The transition to copper interconnects in most high performance IC fabrication has been realized over the past several years. The continuous shrinking of geometrical parameters in the further generation integrated circuits requires an even thinner diffusion barrier that is more effective in stopping copper from diffusing through.

The barrier materials that have been studied include Ta, TaN, Ti–Si–N and Ta–Si–N [1–3]. The selection of the ternary metal-

silicon-nitrides was believed to be based on their increased diffusion activation energy due to their high inter-atomic binding energies [4,5]. These properties are essential to adequate performance in 100 nm device generation. The Ti–Si–N system formed by plasma enhanced chemical vapor deposition (PECVD) has been shown to possess the necessary electrical, chemical, structural and thermal properties and has been successfully integrated in sub-130 nm copper/low-*k* semiconductor device technology nodes [6].

Thermal stability is an important feature of a film to be used as diffusion barrier in advanced technology. This paper presents the results of a study to characterize the barrier performance of the Ti–Si–N formed by a new process of low frequency, high density inductively coupled plasma implantation [7]. Preparation and characterization of the Ti–Si–N films were reported in an earlier work [7]. In the current work, the focus was on the diffusion performance of copper in the barrier films after annealing at high temperatures. The improved barrier performance compared to the conventional TiN film is contributed to the relative difficulty of forming Cu based compounds by Si.

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The sudden drop of the sheet resistance due to Cu compound formation provides an indication of barrier failure.

2. Experimental

Fifty nanometers of Ti_xSi_y film was fabricated by depositing a layer of Ti on silicon wafers first, followed by rapid thermal annealing at 750 °C (RTA1) and 850 °C (RTA2). High density nitrogen implantation into Ti_xSi_y film was conducted in a low frequency inductively coupled plasma (ICP) reactor. The base pressure prior to film deposition was 6.4×10^{-5} Torr. Low frequency ~ 0.5 MHz has been applied for the inductive plasma production. The nitrogen plasma treatment time was chosen to be 30 min and the argon gas flow rate was 30 sccm. The total gas pressure was maintained at 2×10^{-2} Torr, the substrate temperature was 250 °C during the plasma processes and the plasma power was 2000 W.

To evaluate the performance of ICP Ti–Si–N as a copper diffusion barrier, 150 nm thick copper film was sputter deposited onto the Ti–Si–N layer. The resulting stacks were annealed in nitrogen ambient at 350, 450, 550, 650, 750 and 850 °C for 30 min. After annealing, the copper was stripped off in a solution containing 260 g/l ammonium persulfate ($(NH_4)_2S_2O_8$) in H_2O . The depth profile of Cu, Ti, Si and N in the structures after annealing was characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) with 3 keV Ar^+ ion primary beam at a beam current of 50 nA.

The surface morphology of the samples was observed using field emission scanning electron microscopy (FESEM) at a voltage of 5 kV and a beam current of 12 μA . Elemental mapping was carried out using energy dispersive X-ray (EDX). The phase composition was investigated using X-ray diffraction. The sheet resistance was measured using ResMapTM four-point probe system.

3. Results and discussion

As reported in early work [7], the Ti–Si–N film consisted of a mixture of TiN and Si_3N_4 phases. Fig. 1 presents the ToF-SIMS depth profile of Cu/Ti–Si–N/ Ti_xSi_y /Si structure without

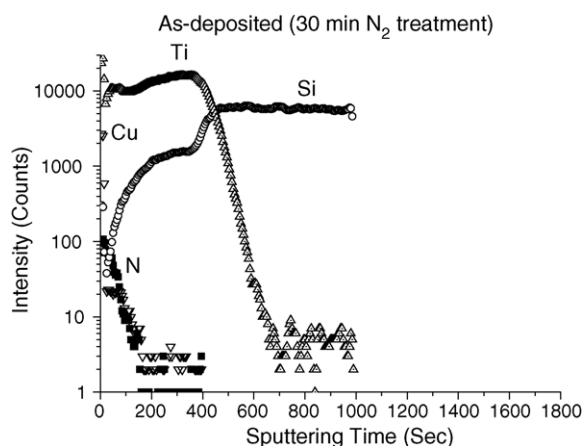


Fig. 1. SIMS depth profile of Cu, Ti, Si and N for as-deposited sample without annealing. No sign of copper diffusion is observed.

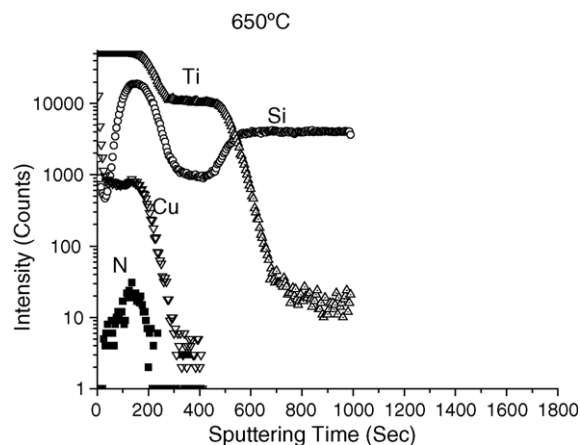


Fig. 2. SIMS depth profile of Cu, Ti, Si and N after annealing for 30 min at 650 °C. Copper diffused into Ti–Si–N film.

annealing. An abrupt gradient in copper depth profile was observed which shows no sign of copper diffusion through the Ti–Si–N film. The profile of this sample was used as a reference for the Cu diffusion study in annealed samples. Fig. 2 shows that copper had diffused into the 15-nm thick Ti–Si–N film after annealing for 30 min at 650 °C. Below this temperature, no copper diffusion was found for the samples that were annealed at 350, 450 and 550 °C. Fig. 3 is the profile at 550 °C, which is similar to the profile of as-prepared sample in Fig. 1.

When the samples were annealed at 750 and 850 °C in nitrogen ambient for 30 min, significant diffusion of copper into Ti–Si–N film was observed. Fig. 4 shows a typical profile for annealed samples at 850 °C. Fig. 5 shows the XRD measurement of as-deposited samples and annealed samples at various temperatures. For up to 550 °C annealing, only three phases, TiN, Ti_5Si_3 and $TiSi_2$, are present. No copper compounds were found in samples annealed up to 550 °C. These results matched well to the SIMS results.

Carefully analyzing Fig. 5, it was found that when the annealing temperature increased from 350 to 850 °C, the intensities of $Ti_5Si_3(2\ 1\ 0)$ and $TiN(1\ 1\ 1)$ gradually decreased. With the disappearance of Ti_5Si_3 and TiN phases at 750 °C and

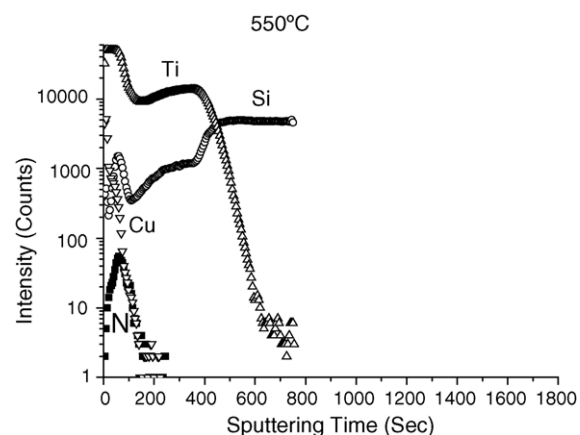


Fig. 3. SIMS depth profile of Cu, Ti, Si and N after annealing for 30 min at 550 °C.

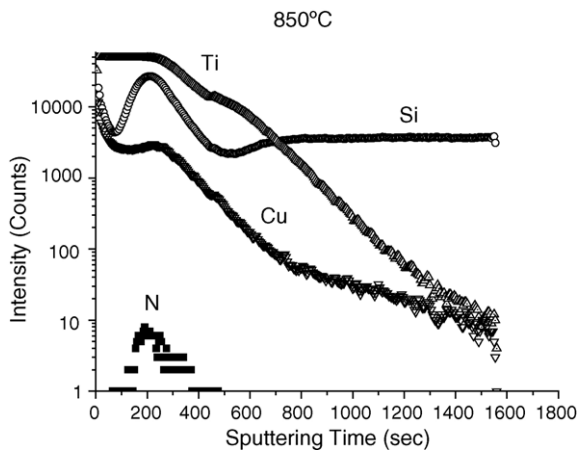


Fig. 4. SIMS depth profile of Cu, Ti, Si and N after annealing for 30 min at 850 °C. Significant copper diffusion into Ti–Si–N film is observed.

above, several Cu–Ti phases and CuN_3 appeared. The results show that the diffusion of Cu into the barrier layer is mainly driven by the reaction of Cu with Ti and N in the film.

Fig. 6 shows the FESEM surface morphology of as-deposited samples. Regions of ridges and valleys were found on the surface. Surface roughness was found to be 20 nm (RMS) by AFM measurement. EDX detected only Ti, Si, N and O in samples annealed at and below 550 °C. The existence of oxygen was due to the exposure of the samples in environment after removing the sample from the vacuum chamber. When the annealing temperature increased to 650 °C, the reaction products were clearly revealed by FESEM. The micrograph in Fig. 7 shows tiny white reaction particles on the Ti–Si–N surface. The larger bright particles in Fig. 8 provide clearly evidence of the reaction, which appears to occur preferentially on the “ridges” of the film. The two graphs show that with

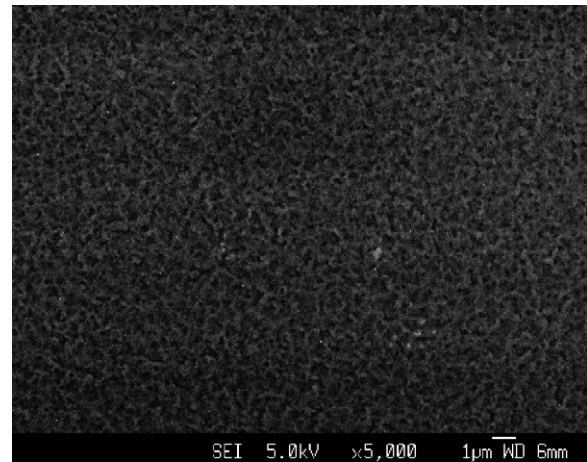


Fig. 6. FESEM surface morphology of as-deposited samples. Ridges and valleys are observed.

increasing annealing temperature, these reaction products grow in size and start to spread to other regions.

Fig. 9 presents a micrograph with the element mapping of a sample annealed at 850 °C for 30 min. It clearly showed that the compounds in the ridges consisted of mainly copper and titanium. Fig. 9(d) shows that no silicon signal was detected on the reaction particles. The results, coupled with the XRD measurement as discussed above, enable us to conclude that the reaction products are mainly Cu–Ti and Cu–N, formed preferentially in the ridges of the Ti–Si–N barrier.

Since the annealing temperature was well below the Tammann temperature, it is reasonable to believe that diffusion of Cu goes preferably through the grain boundaries in ridge regions. Comparing Figs. 7 and 8, the small white particles form first in the ridge areas. The large white particles in Fig. 8 only appear at 850 °C annealing, which are results of growth of

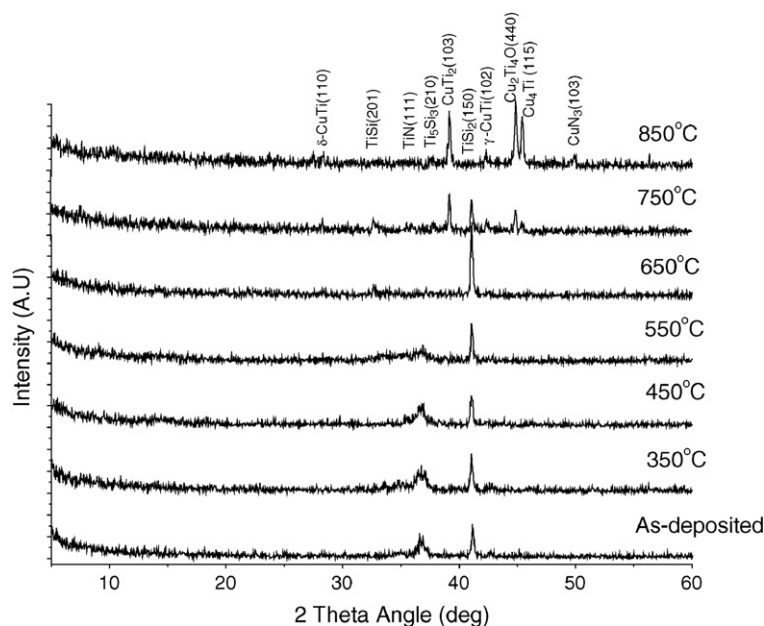


Fig. 5. XRD measurement of the samples after annealing at various temperatures. Cu–Ti and Cu–N compounds are formed at high temperature indicating the diffusion of copper into Ti–Si–N barrier film.

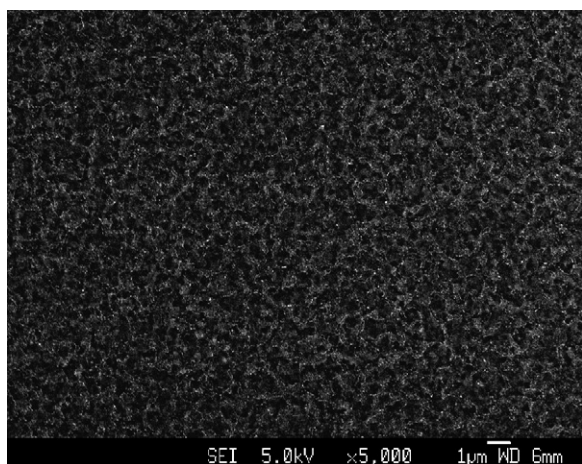


Fig. 7. FESEM surface morphology of the samples after annealing for 30 min at 650 °C. Some compounds are formed on the ridges of Ti–Si–N film.

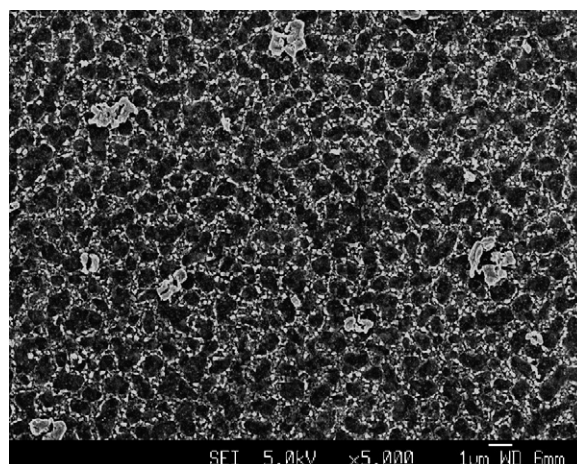


Fig. 8. FESEM surface morphology of the samples after annealing for 30 min at 850 °C. Those compounds formed on the ridges can be clearly observed.

small Cu particles. This picture of diffusion is proposed based on the observations made so far; experimental work is still on-going to identify the phase composition and the grain boundaries in the ridge area using high resolution transmission electron microscope.

Fig. 10 plots the sheet resistance of the samples as a function of annealing temperature. For the as-deposited sample, the sheet resistance was 5.8 Ω/Sq . This value maintained up to 450 °C annealing. There was a slightly increase in the sheet resistance

to a value of 7.3 Ω/Sq when the annealing temperature increased to 550 and 650 °C. This was probably due to the existence of high resistivity TiSi_2 phase in the samples. As shown in Fig. 5, there was an increase in the intensity of TiSi_2 phase at annealing temperature of 550 and 650 °C. There was a sudden drop of the resistance when the annealing temperature was increased to 750 and 850 °C. This corresponded to the formation of Cu–Ti and Cu–N compounds at high temperatures. The reactional diffusion of copper into the Ti–Si–N film decreased

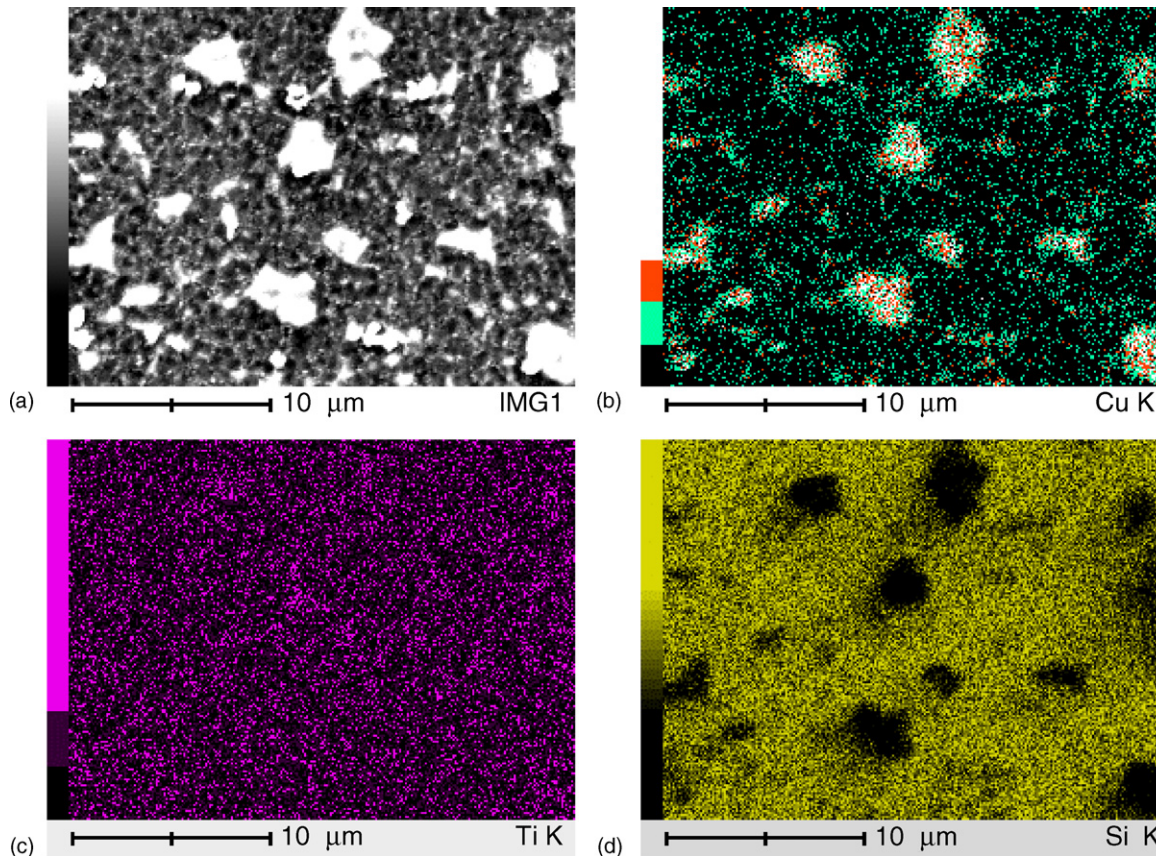


Fig. 9. (a) SEM surface morphology of the samples after annealing at 850 °C for 30 min. (b) Element mapping of Cu. (c) Element mapping of Ti. (d) Element mapping of Si. The mapping indicates that compounds consist of mainly Cu and Ti. Si did not participate in the compound formation.

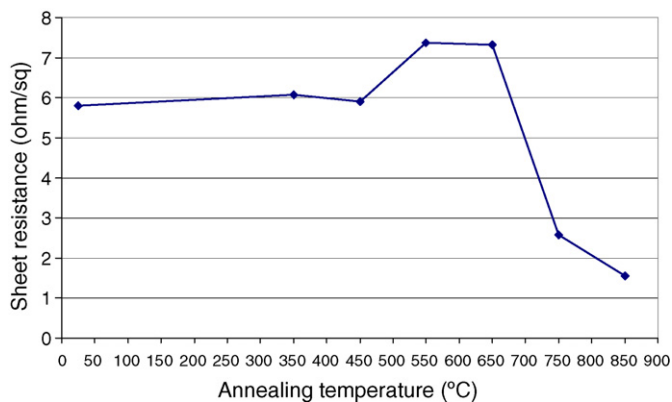


Fig. 10. Sheet resistance of the samples after annealed at various temperature. It is suspected that low resistivity compounds are formed after annealing at 750 and 850 °C.

the overall sheet resistance. The result suggests that a sudden drop in the surface resistance could be used as an indication of Cu diffusion in Ti–N based barriers, including TiN and Ti–Si–N.

Considerable effort has been spent on the barrier performance of TiN films against thermal diffusion of Cu [8–16]. It was generally accepted that the failure was caused by copper diffusion through the grain boundaries of TiN to form copper compounds [13–16]. However, the reported failure temperatures differ among researchers, ranging from 400 to 850 °C [8–12]. The difference in failure temperature might be due to the difference in film microstructure, film thickness, annealing time and the failure criteria used by the researchers. In the work by Moriyama et al. [13], for example, Cu₃Si formation detected by XRD was used as the onset time for diffusion failure of the 25 nm TiN film deposited on Si substrate. They reported no Cu₃Si formation at and below 850 °C annealing for 30 min. This agrees with the current observation that no Cu–Si compounds were detected for up to 850 °C annealing. However, the formation of Cu–Ti and Cu–N compounds was not found in their work, which could be the reason for such a high barrier failure temperature. In most of other research on different types of barrier, such as W, Ta, WN, TaN, the barrier can only prevent Cu diffusion at temperatures below 600 °C (refer to the summary in Ref. [13]).

4. Conclusions

Copper diffusion barrier studies on 15 nm thick ternary Ti–Si–N thin film, prepared by low frequency, high density

inductively coupled plasma process, indicated that barrier failure did not occur until annealing at 650 °C for 30 min. With the diffusion of copper into Ti–Si–N film at high annealing temperatures, Cu–Ti and Cu–N compounds formed. The formation of these compounds caused a significant reduction in sheet resistance from 5.8 Ω/Sq for as-deposited film to 1.5 Ω/Sq for the film after annealed at 850 °C. FESEM and EDX results showed that the compounds formed preferably on the ridge areas. No Si–Cu was found in the current study for up to 850 °C annealing. This implies that the addition of Si contributes to the improvement in the diffusion barrier performance. Based on the overall requirements, the 15-nm Ti–Si–N layer formed by low frequency, high density inductively coupled plasma process in the current study presents an attractive route to produce effective barrier materials against copper diffusion.

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