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The effect of oxygen on the interfacial reactions of Cu/TaN_x/Si multilayers

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Abstract

Interfacial reactions of Cu/TaN_x/Si and silicon nitride/Cu/TaN_x/Si multilayers after thermal treatment at 500 and 700°C under an ambient with residual oxygen were investigated using an energy-filtered TEM (EFTEM). The Cu and TaN_x films were deposited onto the Si (0 0 1) wafer by ionized metal plasma (IMP) technique. An interlayer of TaO_xN_y was observed between Cu and TaN_x diffusion barrier in the Cu/TaN_x/Si sample after 500°C annealing. It is evident that oxygen diffused through the Cu grain boundaries and promotes the oxidation of the Ta nitride barrier layer to form the TaO_xN_y. It is also found that the as-deposited TaN_x ($x \sim 0.5$) film with nano-crystalline microstructure would transform into Ta_2N structure with large grain character after 500°C heat treatment. After 700°C annealing, not only the TaN_x barrier layer transformed into Ta_2N but the silicidation of Cu to Cu_3Si and TaN_x to Ta_5Si_3 occurred. However, no TaO_xN_y interlayer was observed. This may result from the preferable oxidation of Cu_3Si that may suppress the oxidation of TaN_x. Nevertheless, in the silicon nitride capped (silicon nitride/Cu/TaN_x/Si) case, there was no TaO_xN_y interlayer observed in the 500°C annealed specimen. And the interfacial reaction in the silicon nitride/Cu/TaN_x/Si annealed specimen at 700°C also showed much less severe extent than the sample without capping. Experiments show that the oxygen in the ambient enhances the oxidation at 500°C and silicidation at 700°C.

Keywords: Cu metallization; Diffusion barrier; Oxidation; Transmission electron microscopy

1. Introduction

Copper has lower resistivity (1.68 μΩ cm) and much better electromigration resistance compared with Al alloys [1]. Therefore, it is used to replace the Al alloys as the metal wires of interconnect for the next generation ULSI device. However, Cu reacts easily with Si to form copper silicide even at temperatures below 200°C and diffuses very fast in SiO_2 matrix [2,3], therefore, a diffusion barrier is needed to isolate the inter-diffusion behavior. Nicolet [4] has summarized that a diffusion barrier must meet several requirements such as prevention of metal atom diffusion, low resistance, and good adhesion to Si substrate and dielectric materials. Among the various barrier materials for copper metallization, Ta, Ta–N and Ta–Si–N alloys have received the most intensive study due to their high melting points, and no reaction with Cu, as well as relatively good adhesion to SiO_2 [5,6]. It is well-recognized that there are several factors such as impurities, defects, thickness, and stress affecting the performance of diffusion barrier [7–10]. However, in most studies, the device after Cu metallization is usually annealed in high vacuum ($<10^{-7}$ Torr) and no one has yet discussed the ambient effect on the performance of the diffusion barrier in low vacuum annealing. High vacuum annealing is effective but is a relatively expensive process compared with the low vacuum one with Ar atmosphere. The ambient with residual oxygen in low vacuum annealing may affect performance of the nitride barrier such as in the case of an oxygen stuffing process for TiN barrier [11]. This stimulates us to study the oxygen effect on the thermal stability of TaN barrier. In this study, we investigated the thermal stability of Cu/TaN_x/Si and silicon nitride/Cu/TaN_x/Si multilayers in ambient containing residual oxygen in order to understand the effect of oxygen on the interfacial reactions.

2. Experimental

The Cu and TaN_x (x is slightly <0.5) films were deposited on 8 in (0 0 1) silicon wafers in an Applied Materials Electra™ system that utilized ionized metal plasma (IMP)

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Table 1
The experimental parameters used for elemental mapping

Element	Energy position (eV)	Energy window (eV)	Background model
Si	99	5	Exponential
N	401	20	*R*-power law
O	532	30	*R*-power law
Cu	931	30	*R*-power law

processing technology [12]. The N_2 partial flow for TaN_x deposition is about 10–15% mixed with Ar gas. The base pressure of the IMP chamber was typically $\sim 10^{-8}$ Torr. The stacking sequences and thickness of the deposited films were Cu (150 nm)/TaN_x (25 nm) on Si wafers. The silicon nitride capped layer in 20 nm thick was deposited by plasma assisted chemical vapor deposition.

To investigate the interfacial reactions in thermal treatment, samples were treated in a vacuum furnace at 500 and 700°C in purified Ar (4N) atmosphere. All samples were cut into 1 cm × 1 cm, before being put into the furnace. Annealing time at each temperature was 30 min. Before feeding with Ar gas, the furnace was purged several times with Ar, and evacuated to 10^{-2} Torr range. From the leaking test, the partial pressure of residual oxygen was estimated to be about 10^{-4} Torr.

Wedge method [13] for grinding and polishing has been used for cross-sectional TEM specimen preparation. The final step is ion milling to perforation. Mo or Ni grids were used for mounting TEM specimens to avoid the interference of EDX signal from Cu grid with that from the Cu film in the samples. A JEOL 2010F field-emission-gun TEM, equipped with an X-ray energy dispersive spectrometer (EDS) and a Gatan Imaging Filter was used to study the microstructures and chemical compositions. Elemental mapping was carried out using the three windows method [14]. Table 1 shows the experimental parameters for the elemental mapping method. Nano-beam diffraction (NBD) and EDS was performed with a probe size <1 nm. The observation of Ta M-edge (1735 eV) and the Ta O-edge (37 eV) is obscured with the ghost peak of field emission gun [15] and the plasmon peaks caused by multiple scattering, respectively, so, it is difficult to obtain the true elemental map of Ta. Therefore, EDS did the characterization of Ta in this work.

3. Results and discussion

The as-deposited TaN_x (x is slightly <0.5) layer has a nano-crystalline structure that is the same as reported previously by Chin [16]. In as-deposited sample, the average sizes of the Cu grains and TaN_x grains are approximately 1 μm and 5 nm, respectively, and no interlayer was observed in the interfaces of Cu/TaN_x and TaN_x/Si. Fig. 1(a) shows that a cross-sectional TEM image of a 500°C heat-treated sample. There is an interlayer with thickness of about 1–2 nm between Si and TaN_x. Its composition was identified to be Ta and Si from the analyses of EDS and EELS in Fig. 1(b) and (c). The energy difference between Si-K peak (1.74 keV) and Ta-M peak (1.71 keV) in Fig. 1(b) of the EDS spectrum is 0.03 keV that does not allow the Si to be unambiguously identified. The existence of Si was confirmed from the EELS spectrum in Fig. 1(c). No O and N signals can be detected from the EELS spectrum. Such an amorphous Ta silicide was often observed in Ta/Si samples after annealing at temperatures above 500°C [17]. No Cu silicides were found at TaN_x/Si interface, implying that no Cu penetrated into Si during 500°C annealing. However, the structure of TaN_x diffusion barrier with a nanocrystalline structure has transformed to crystalline Ta_2N structure with grain size larger than 500 nm in lateral dimensions after 500°C annealing. A diffraction pattern of $[1\,\bar{1}\,0\,0]$ of Ta_2N from the barrier layer is shown as an inset of Fig. 1(a). Furthermore, an interlayer of about 3 nm thickness was observed at the Cu/Ta_2N interface. An inset NBD pattern in Fig. 1(a) shows this interlayer is an amorphous structure. The EDS spectrum of this amorphous interlayer in Fig. 1(d) shows this amorphous layer contains Cu, O and Ta. No N signals were detected in the EDS due to the strong absorption effect of Ta. The appearance of Cu signals in the spectrum is due to the effect of beam broadening which gives rise to a 5 nm diameter size according to the calculation [18] using the thickness data measured from the intensity of the EELS plasmon peak [19]. The EELS technique, on the other hand, offers the spatial resolution of about 1–2 nm which is better than that of EDS [20]. Fig. 1(e) shows the EELS spectrum of interlayer with energy ranges from 350 to 600 eV. Two edges were observed at about 401 and 532 eV which are identified to be N and O, respectively. No Cu edge at 931 eV can be observed in the interlayer. Therefore, it is believed that the interlayer at the Cu/TaN_x interface is the amorphous TaO_xN_y structure. It was reported previously by other researches that TaO_xN_y forms as a result of the surface oxidation of TaN [21,22]. The study of the thermal stability of Cu/Ta/Si structure, by Yin et al. [23], has also shown that oxygen can diffuse through Cu grain boundaries and react with Ta barrier layer to form amorphous TaO_x at annealing temperature lower than 600°C. Similarly, the external oxygen can diffuse through Cu grain boundaries and, therefore, result in the formation of TaO_xN_y between the Cu and TaN_x layers in the present case.

Fig. 2 shows the cross-sectional TEM image of silicon nitride/Cu/TaN_x/Si sample after thermal annealing at 500°C. The nanocrystalline TaN_x structure has been also transformed to Ta_2N structure with larger grain size of about 500 nm. However, the interface between Cu and Ta_2N barrier layer is flatter than that in the Cu/TaN_x/Si case. Neither TaO_xN_y interlayer nor Cu silicide was found in this capped sample at the Cu/TaN_x interface. One may argue that the alternation of the behaviors of diffusion and reaction in the capped case may be due to the stress from the capped layer [24]. It has been reported that the stress from silicon nitride is tensile stress [25] which can enhance the diffusion and

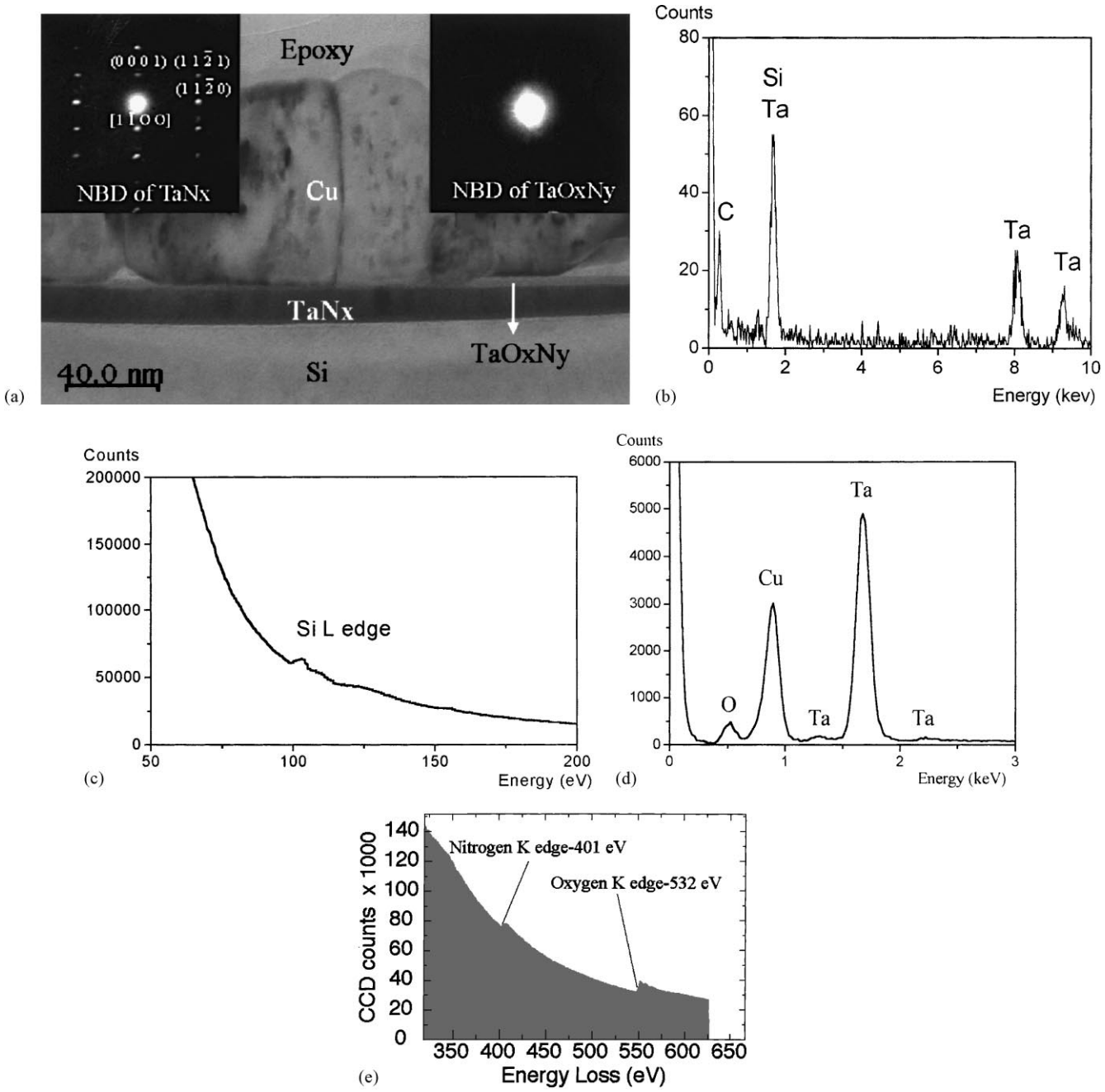


Fig. 1. (a) Cross-sectional TEM image after thermal annealing at 500°C obtained from a Cu/TaN_x/Si sample. The insets are diffraction patterns from the TaN_x barrier and the interlayer between Cu and TaN_x. (b) EDS spectrum obtained from the interlayer between TaN_x and Si. (c) EELS spectrum obtained from the interlayer between TaN_x and Si. (d) EDS spectrum obtained from the amorphous interlayer between TaN_x and Cu. (e) EELS spectrum obtained from the amorphous interlayer between TaN_x and Cu.

silicidation [26,27]. In the present case, no stress measurement was made. Nevertheless, it may be reasonable to believe that the main role of the capped layer of silicon nitride is to stop diffusion of oxygen through the Cu grain boundaries effectively from the chamber source in this case.

After 700°C heat treatment, a Cu/TaN_x/Si sample exhibited in grey color under optical microscope observations, indicating that severe reactions occurred during annealing, and its microstructure was shown in Fig. 3(a). A reacted phase of the size about ~2 μm surrounded by an amorphous layer was found in the Si substrate. The new phase formed is identified to be η''-Cu_3Si, which has a long period structure as analyzed from diffraction patterns shown as an inset in Fig. 3(a), and the surrounded amorphous layer, is identified to be Cu–Si oxide by EDS analysis in Fig. 3(b). The C signal in the EDS spectrum arises from the contamination of carbon on the surface of sample. Reaction of Si with Cu to form η''-Cu_3Si phase could take place

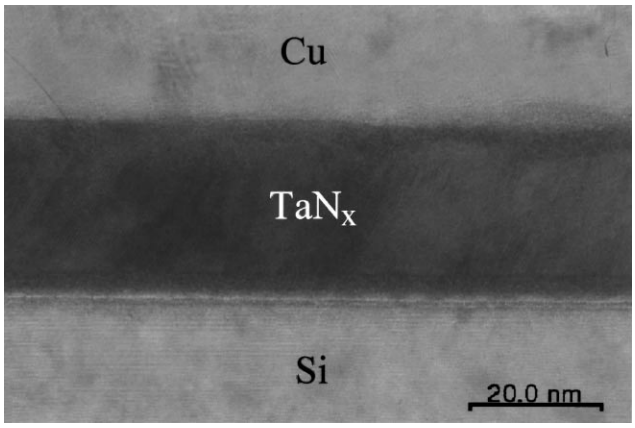
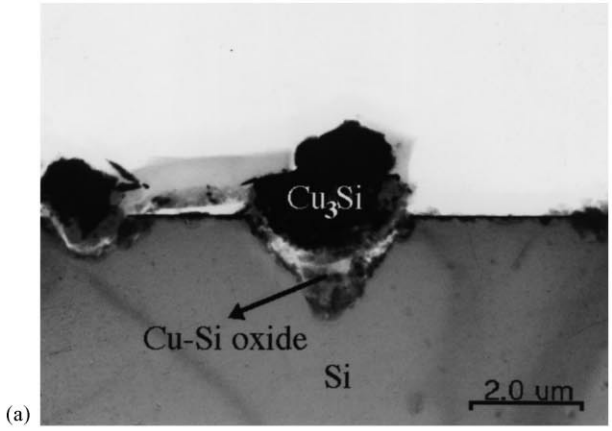
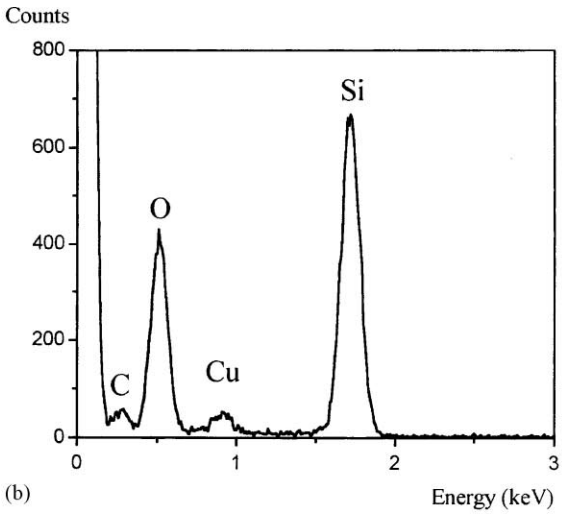


Fig. 2. Cross-sectional TEM image of a silicon nitride/Cu/TaN_x/Si sample after thermal annealing at 500°C.

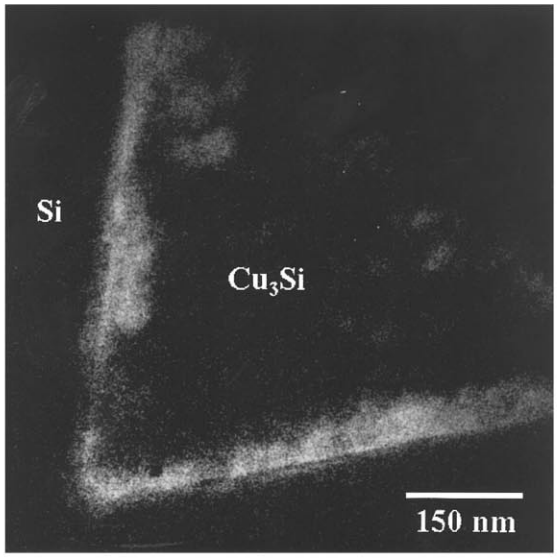
at about 200°C [2]. The η''-Cu_3Si phase contains high densities of stacking faults and vacancies [28]. It has been reported that the η''-Cu_3Si may catalyze the oxidation of Si due to its high density of defects [29,30]. Oxygen from the ambient gas can also diffuse through Cu_3Si and then to form silicon dioxide layer along the interface of Cu_3Si/Si. An oxygen elemental map in Fig. 3(c) shows formation of SiO_2 inside Cu_3Si that may be a starting point of catalyzing process; oxidation of Cu_3Si will produce SiO_2 and release free Cu to form new Cu_3Si. The process can iterate itself until all the Cu are consumed. It is therefore believed that formation of η''-Cu_3Si may promote the penetration of Cu through the reacted barrier layer into Si substrate and to form Cu silicide. Fig. 3(d) is a magnified image from this sample that shows two interlayers between Ta_2N and Si. The layer above Si has an amorphous structure



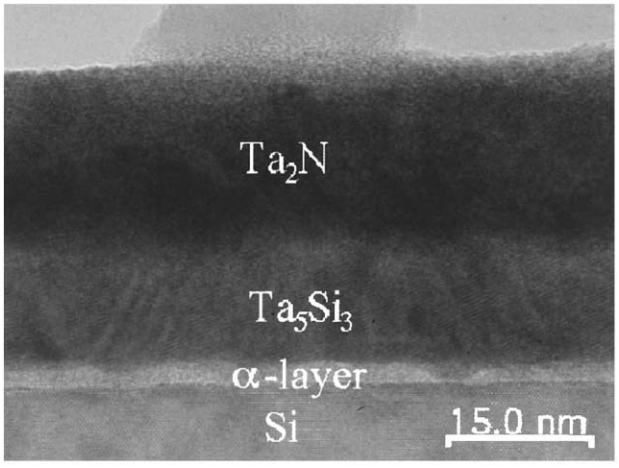
(a)



(b)



(c)



(d)

Fig. 3. (a) Cross-sectional TEM image after thermal annealing at 700°C obtained from a Cu/TaN_x/Si sample. (b) EDS spectrum obtained from an area of SiO_2 surrounding the Cu silicide. (c) Oxygen elemental map of a Cu_3Si from another area. (d) High-resolution TEM image of TaN_x/Si interface obtained from 700°C.

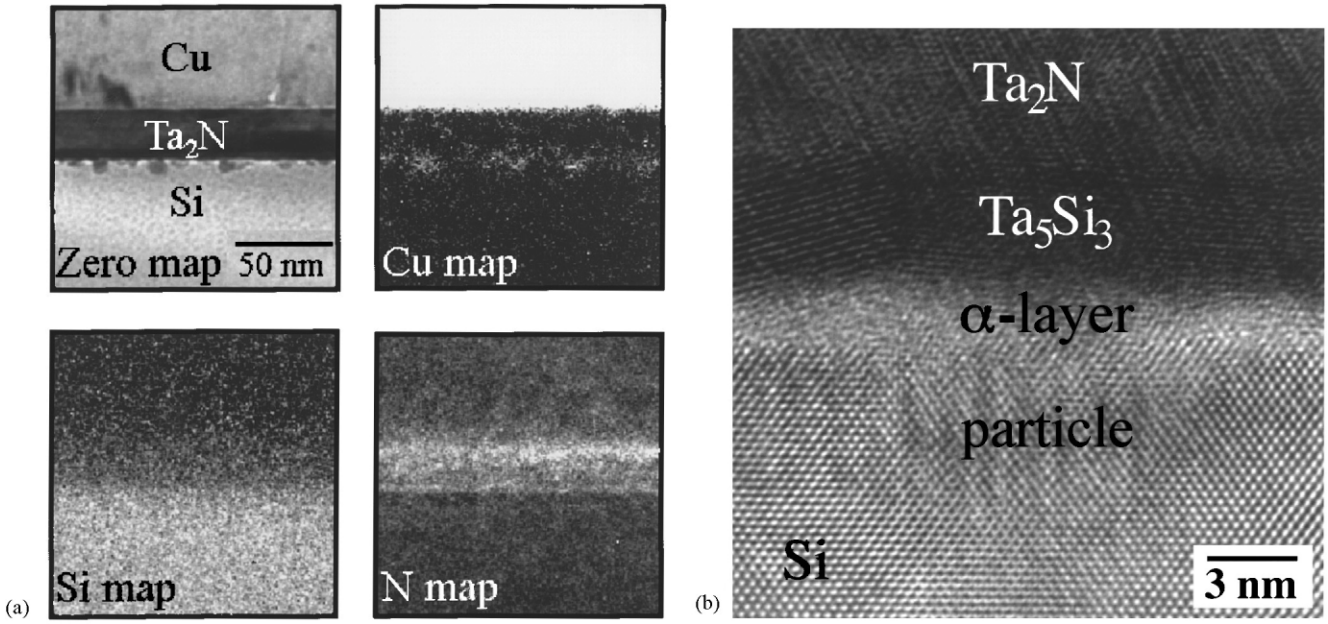


Fig. 4. (a) The EELS maps of a Si nitride capped sample obtained from 700°C: the zero loss map, silicon map, oxygen map, and copper map. (b) High-resolution TEM image of Si nitride capped sample obtained from 700°C showing the interlayers.

with a thickness of 3 nm, and EDS and EELS results show that it contains elements of Ta and Si only. The upper layer is identified as Ta_5Si_3 whose thickness is of about 11 nm. Interestingly, no TaO_xN_y films can be observed upon the Ta_2N film. The reason may be that oxygen reacts actively with Cu_3Si and finally oxygen is strongly bonded with Si to form SiO_2 that is more stable than TaO_xN_y.

Fig. 4(a) shows the four energy-filtered images obtained from the silicon nitride/Cu/TaN_x/Si specimen after 700°C annealing. From the zero loss image, small precipitates with near triangular shape were observed to be embedded in Si substrate underneath the barrier layer. The average size of these particles is of about 10 nm. Elemental map of Cu reveals that these particles contain Cu. This is evidence that Cu has already penetrated through the barrier layer. An HRTEM image of an embedded particle is given in Fig. 4(b). Although Si map shows less bright contrast at the same positions, we are not sure whether these particles are Cu silicide or pure Cu. It was difficult to obtain reliable compositional data from EDS and EELS, since these particles are embedded within the Si substrate and no good NBD pattern was recorded for this sample. However, as the η''-Cu_3Si is preferable to form at the temperature as low as 200°C, we believe that these particle are probably silicide rather than pure Cu. These Cu silicide particles have an average size much smaller than that in the Cu/TaN_x/Si specimen annealed at the same temperature.

The Si map also shows very little of Si diffused into the TaN_x barrier. Clearly, no oxide layer was found in TEM observations, indicating that as in the 500°C case a silicon nitride capped layer can stop effectively the diffusion of oxygen from the ambient and in turn to retard the interfacial reaction at TaN_x/Si interface. Therefore, the major role of the silicon nitride is to isolate the oxygen in the ambient gas. These results could imply that the residual oxygen from ambient should play an enhanced role in the diffusion barrier failure.

Both amorphous silicide and Ta_5Si_3 layers were also observed, which is similar to that in the non-capped sample annealed at the same temperature. However, the thickness of α-layer (2 nm) and Ta_5Si_3 layer (6 nm) of the capped samples are thinner than those in the non-capped samples. The Ta_2N layer in the non-capped sample is about 19 nm thick which is smaller than that 22 nm in the capped sample. The microstructures of both capped and non-capped samples at this temperature are similar to those reported by Holloway et al. [31]. Hence, we may conclude that the extent of failure at 700°C is more severe in the non-capped samples than in the capped ones.

Min et al. [32] have pointed out that there are two major competing failure mechanisms for the Ta–N type diffusion barrier. One is the diffusion of Cu through the grain boundary of TaN barrier layer into Si substrate to form Cu silicide for the TaN barrier layer which remains stable during the whole process. The other is the interfacial reaction taking place between the Ta-rich barrier layer (such as Ta_2N) and Si substrate. In the silicon nitride capped sample, the failure mechanism resembles the interfacial reaction in which case the Ta silicide Ta_5Si_3 forms. The ambient containing residual oxygen promotes this silicidation reaction in non-capped sample so that the Ta silicide is thicker. This result is in good agreement with a previous report [33] that the oxygen ambient can enhance out-diffusion of Si. Oxidation of $TaSi_2$/Si also shows similar enhanced diffusion behavior of Si [34].

Therefore, it is thought that oxygen could affect the behavior of interfacial reaction for the Cu/TaN_x/Si. In essence, the major role of the silicon nitride capped layer is to isolate the sample from exposure of oxygen ambient, though the effect of residual stress from the silicon nitride capping can not be completely excluded.

4. Conclusions

The oxygen effect on the interfacial reactions of Cu/TaN_x/Si and silicon nitride/Cu/TaN_x/Si structures after thermal annealing has been investigated by EFTEM. Based on the above results, we conclude as follows:

1. Oxygen ambient promotes the oxidation of Ta nitride barrier layer at 500°C, but it may not enhance the intermixing of Ta and Si (forming amorphous TaSi layer) at 500°C. An interlayer of TaO_xN_y was observed in the Cu/TaN_x/Si specimen between Cu and the barrier layer after 500°C annealing. However, no such oxide interlayer was observed in the silicon nitride/Cu/TaN_x/Si specimen. It is evident that oxygen can diffuse through Cu grain boundaries to oxidize the TaN_x layer.
2. Silicidation of Ta (amorphous Ta silicide and Ta_5Si_3) and Cu in the Cu/TaN_x/Si sample were more severe than the silicon nitride/Cu/TaN_x/Si sample after 700°C heat treatment due to the ambient effect of oxygen.

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