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Copper diffusion barrier performance of amorphous Ta–Ni thin films

Hua Yan[a,b], Yee Yan Tay[a], Yueyue Jiang[a], Natalia Yantara[a], Jisheng Pan[c], Meng Heng Liang[a], Zhong Chen[a,*]

[a] *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*
[b] *Globalfoundries Singapore, 60 Woodlands Industrial Park D Street 2, Singapore 738406, Singapore*
[c] *Institute of Materials Research & Engineering, ASTAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Singapore*

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ABSTRACT

Amorphous Ta–Ni thin films were deposited on Si substrate by magnetron sputtering. The oxygen concentration was adjusted by controlling the substrate bias during the sputtering deposition. Two types of Ta–Ni films, namely $Ta_{67.34}Ni_{27.06}O_{5.60}$ and $Ta_{73.25}Ni_{26.10}O_{0.65}$ were employed in the current study. To assess the diffusion barrier performance, Cu/Ta–Ni/Si stacks were fabricated in sequence without breaking the vacuum. The samples were then annealed in vacuum for 30 min at temperatures ranging from 500 °C to 800 °C. SEM, 4-point probe, SIMS and TEM have been used to study the film properties to assess the barrier performance. The films were found to remain stable up to 600 °C without significant Cu diffusion. At 700 °C, Cu diffusion through the barrier film was detected in both types of samples, but with different degree of severity. For the $Ta_{67.34}Ni_{27.06}O_{5.6}$ barrier film, there was no Cu–Si reaction at 700 °C, while Cu_3Si was observed at the $Ta_{73.25}Ni_{26.10}O_{0.65}$/Si interface. At 800 °C, Cu_3Si crystalline phase was found in both samples, and the barrier films have completely lost integrity. This study shows that sputter deposited Ta–Ni amorphous thin films can be used as an effective copper diffusion barrier for microelectronic device fabrication. Incorporation of a few percent of oxygen into the film can retard copper diffusion and interface reaction, which enhances the barrier performance.

1. Introduction

As the development of semiconductor industry is pacing to 45 nm technology node and below, the materials and integration scheme of both front-end-of-line (FEoL) and back-end-of-line (BEoL) has been going through revolutionary changes [1]. In BEoL integration, Cu metallization has been widely used because of its high electrical conductivity and good electromigration resistance. Continued improvement of the circuit performance requires the optimizaiton of the materials selection and process integration. Cu diffuses fast into dielectrics and Si at elevated temperatures, causing degradation of the semiconductor devices [2]. Thus a thin barrier has to be applied between the Cu and dielectrics to prevent Cu diffusion. Currently, a dual layer barrier Ta/TaN is used in the industry, with Ta as an adhesion layer and TaN the barrier to isolate Cu from reaching the dielectrics. Ta-based barrier has shown excellent performance in preventing Cu diffusion at elevated temperatures [3,4]. An added advantage is that the high corrosion resistance of Ta eliminates corrosion related reliability concern [5]. The Ta/TaN bi-layer scheme has proven to be a very successful barrier up to 65 nm technology node. However, in the advanced semiconductor techniques with the increasing metallization layers and circuit density, the resistance–capacitance delay (RC delay) contributed from BEoL has become the controlling factor in limiting the device speed [6]. Thus to reduce the RC delay from BEoL, the resistance of the barrier has to be further reduced. The relatively high resistance of TaN has to be solved in the development of future generation of semiconductor device fabrication.

To reduce the electrical resistance while maintaining good Cu barrier performance, Ta based amorphous alloys, such as Ta–Ni, Ta–Ti and Ta–Cr have been proposed [7]. Amorphous alloy, or metallic glass, has been widely studied in bulk form (bulk metallic glass) [8]. However, its thin film counterparts have received little attention so far. Amorphous structure is free of grain boundaries and thus would eliminate the dominant diffusion channels at low temperatures. Crystalline thin films deposited at low temperatures usually display columnar texture, and the columnar boundaries act as fast diffusion routes, leading to even worse performance than polycrystalline thin films. Therefore employing the concept of amorphous metal alloy has the micro-structural advantage while preserving the good conductivity offered by the constitutive metals.

Amorphous alloys are thermodynamically unstable, thus one of the key concerns is their thermal stability at high temperatures, as it has to be stable above the semiconductor manufacturing peak

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* Corresponding author.
E-mail addresses: aszchen@ntu.edu.sg, zhongchen2006@gmail.com (Z. Chen).

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temperature (400 to 450 °C). To improve the thermal stability of the metallic glass, two or more metals are generally incorporated [9]. A study by Fang et al. [10] showed that Ta–Ni films could prevent Cu reaction with Si substrate at temperatures up to 700 °C, which is comparable with TaN. In our preliminary work, we have also found that Ta based alloy thin films (Ta–Ni, Ta–Ti, and Ta–Cr) generally show lower electrical resistance than TaN. They also exhibit good adhesion with both Cu and dielectrics. Thus these amorphous metallic thin films are promising candidates to replace Ta/TaN barrier as Cu diffusion barrier for future generation of nano electronic devices.

During the study of Ti-based Cu diffusion barrier, it was observed that certain amount of oxygen was incorporated into the films during the plasma vapor deposition process [11–14]. This is due to the strong affinity between Ti and the oxygen residue in the deposition chamber. Similar effect exists for Ta too, as demonstrated in our recent work [15]. Oxygen appears to stabilize Ta diffusion barrier as previously reported [16], and the beneficial effect might be derived from the so called stuffing effect, which is effectively the oxygen segregation at Ta grain boundaries [17] or other easy diffusion channels. Laurila et al. [18] reported formation of TaO_x at Ta(O)/Cu interface at elevated temperature and attributed it as the reason for the enhanced barrier performance. However effect of oxygen on Si/Ta(O) interface was not discussed in the work. In our previous work using sputtered films on Si substrate, we have shown that oxygen addition to the amorphous metallic Ta–Ni films has improved their thermal stability [15]. The interfacial reaction between Ta and Si occurred at 750 °C for low oxygen-containing (<1 at%) Ta–Ni films, while for higher oxygen-containing (∼5 at%) samples, the interfacial reaction was delayed till 800 °C. The difference is related to a more stable Ta–O layer at Ta–Ni/Si interface in oxygen-rich Ta–Ni film. In higher oxygen-containing (∼5 at%) Ta–Ni film, the pre-existing Ta–O layer remained stable at 750 °C, while in low oxygen containing (<1 at%) Ta–Ni films, the Ta–O layer disappeared at 750 °C. The previous study was carried out to evaluate the thermal stability of the thin films only. Cu diffusion assessment was not performed [15]. As existence of oxygen changes the interfacial reaction between Ta–Ni and Si, diffusion of Cu through Ta–Ni barrier and subsequent reaction between Cu and Si could also be delayed with certain amount of oxygen. The previously proposed stuffing effect may also be applicable in the current study, as existence of oxygen in Ta–Ni grain boundary could result in higher Cu diffusion activation energy and lower Cu diffusion rate. Based on this hypothesis, beneficial effect could be obtained when introducing oxygen to Ta–Ni Cu diffusion barrier.

As amorphous Ta–Ni has promising potential as Cu diffusion barrier for BEoL applications, it is of great importance to further understand the Cu diffusion behavior leading to an appropriate assessment of its barrier performance. The failure mechanism of this class of materials will be of great interests too. In the current work, Ta–Ni thin films with different levels of oxygen concentration were deposited on Si substrate. A layer of Cu was then deposited as the top layer without breaking the vacuum. Cu barrier performance was evaluated and compared after annealing. The diffusion process and failure mechanism were studied based on advanced electron microscopic and spectroscopic analyses.

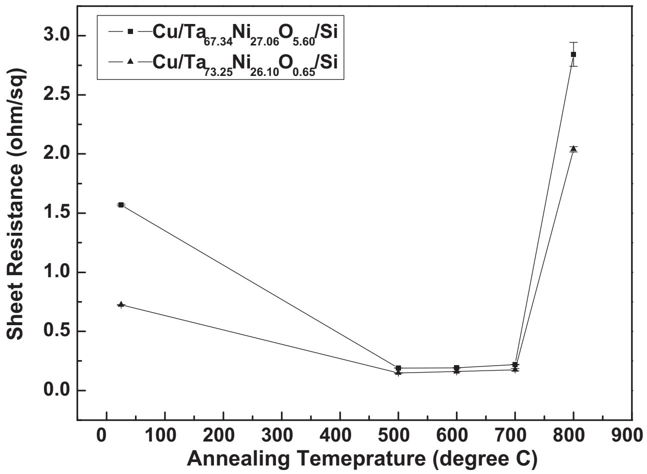

Fig. 1. Sheet resistance of Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si and Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si samples annealed at different temperatures.

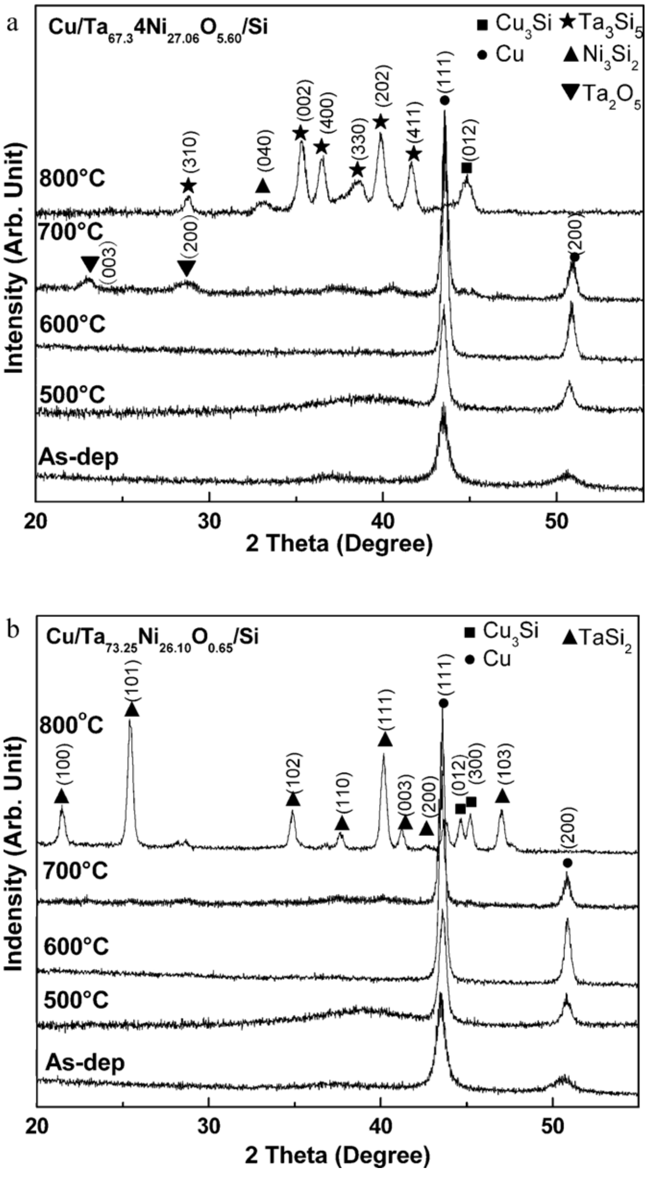

Fig. 2. XRD spectra of (a) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si and (b) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si annealed at elevated temperatures.

2. Experiment

Cu/Ta–Ni/Si stacks were prepared by depositing Ta–Ni and Cu sequentially on Si substrate using a magnetron sputtering machine. The chamber was pumped to 5.32×10^{-4} Pa before deposition. The Ta–Ni films were deposited using co-sputtering of Ta and Ni targets with impurity of 99.999%. Ar gas with pressure of 2.67 Pa was flowed through the chamber during the sputtering. The

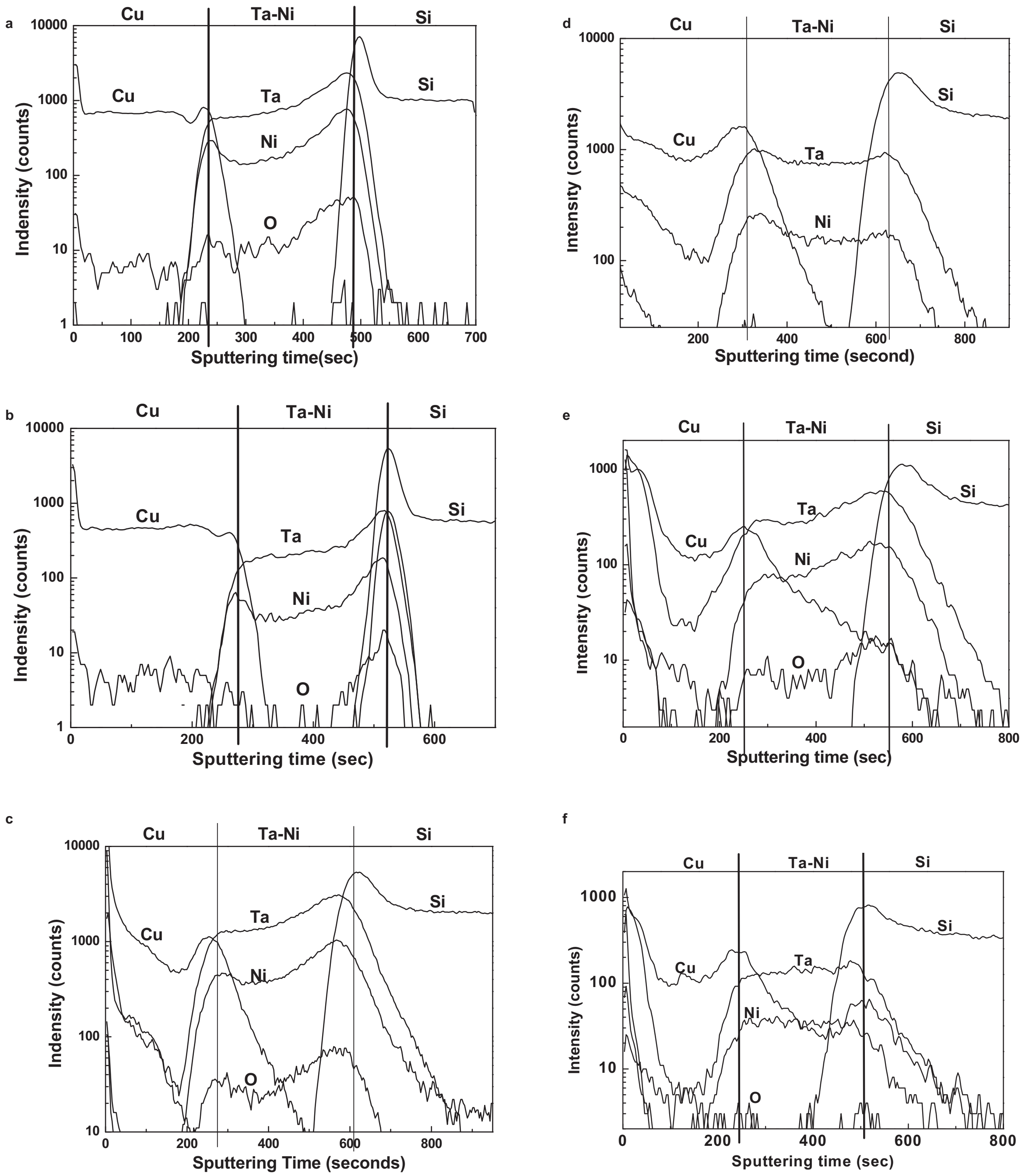

Fig. 3. ToF-SIMS depth profile of elements Cu, Ta, Ni O, Si of (a) as-deposited Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si; (b) as-deposited Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si; (c) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si after 600 °C annealing; (d) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si after 600 °C annealing; (e) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si after 700 °C annealing; (f) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si after 700 °C annealing..

sputtering powers were RF 200 W for Ta and DC 80 W for Ni targets respectively. In order to obtain Ta–Ni films with different oxygen concentration, RF bias of 0 W and 100 W were applied on the Si substrate during deposition. The thickness of the Ta–Ni layer was controlled to be around 100 nm in all samples. A 200 nm thick Cu layer was then deposited on the Ta–Ni with DC power of 200 W without breaking the vacuum. Sample holder was rotated to ensure film uniformity during the sputtering.

To study the thermal stability and microstructure evolution of the Ta–Ni films, the samples were annealed in vacuum at a base pressure of 1.33×10^{-3} Pa at temperatures up to 800 °C for 30 min. Electrical conductivity was measured using a 4-point probe system. The composition was measured using energy dispersive X-ray spectrometer (EDX) attached with SEM. The depth profiles of film composition were characterized using a secondary ion mass spectroscopy (SIMS). The film crystalline phases were determined by X-ray diffraction (XRD) using a Rigaku diffractometer. The interfacial stability and microstructure evolution of the film stacks were examined using a JEOL 2100F high resolution transmission microscope (HRTEM) with EDX attachment.

3. Results and discussion

Ta–Ni films with zero bias (0 W) resulted in corporation of around 5.6 at% of oxygen, the sample is thus named as $Ta_{67.34}Ni_{27.06}O_{5.60}$ based on the composition. Applying 100 W bias largely prevented oxygen incorporation, leading to the film composition $Ta_{73.25}Ni_{26.10}O_{0.65}$. The effect of applying bias during

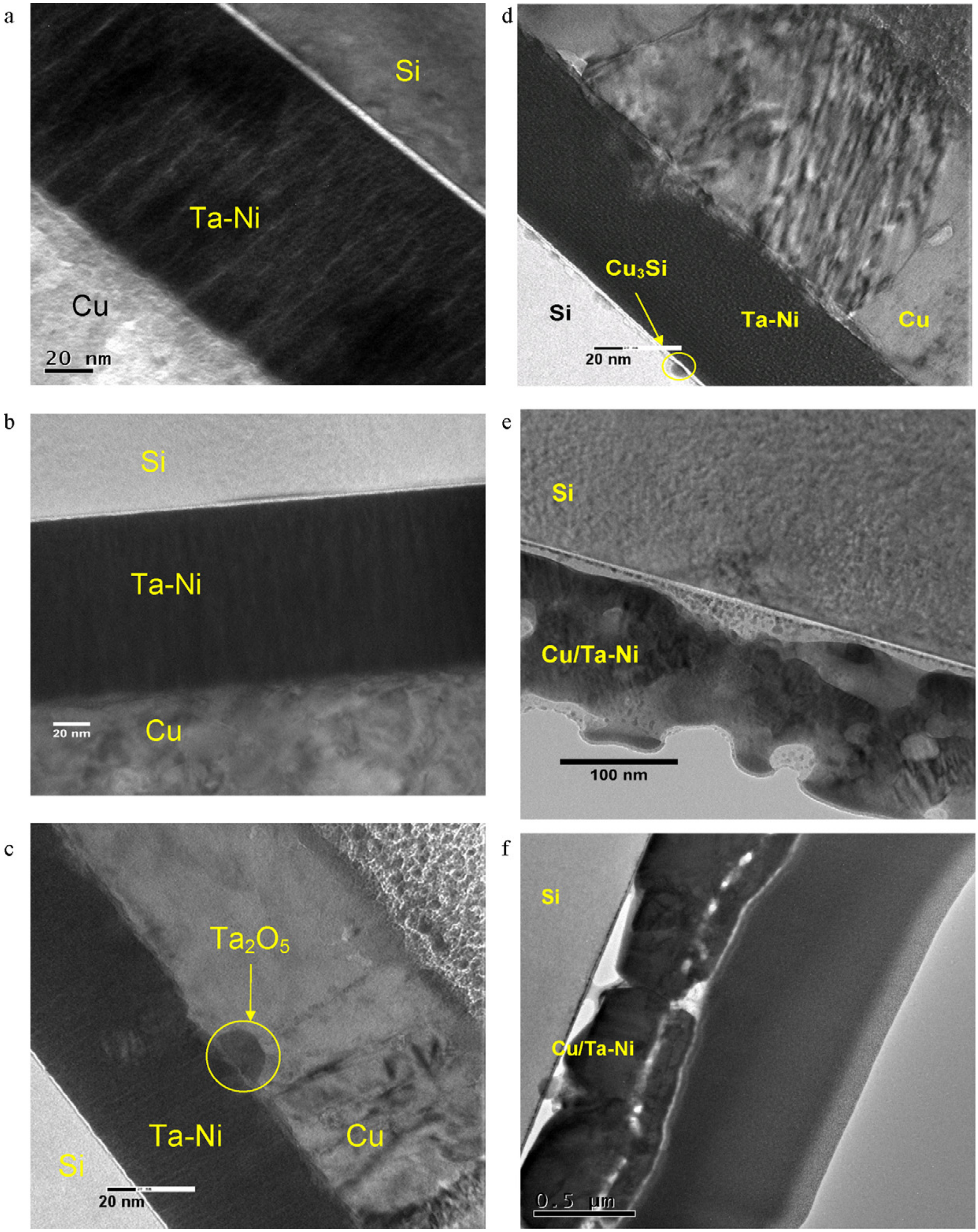

Fig. 4. TEM micrograph of (a) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si after 600 °C annealing; (b) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si after 600 °C annealing; (c) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si after 700 °C annealing; (d) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si after 700 °C annealing; (e) Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$/Si after 800 °C annealing; (f) Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$/Si after 800 °C annealing.

deposition on the film composition has been discussed in previous work [15].

The sheet resistance of the Cu/Ta–Ni/Si samples at room temperature and after annealing at temperatures from 500 °C to 800 °C is shown in Fig. 1. Five to ten readings were taken for each measurement, the mean values and the standard deviations are plotted. At the as-deposited state, the sheet resistance of Cu/$Ta_{67.34}Ni_{27.06}O_{5.60}$ was higher than that of Cu/$Ta_{73.25}Ni_{26.10}O_{0.65}$. The difference is mainly due to the presence of oxygen. Indeed in our previous work, we found that resistivity of two films with similar compositions at the as-deposited state was 411 µΩ cm for $Ta_{66.33}Ni_{28.42}O_{5.25}$ and 217.29 µΩ cm for $Ta_{72.02}Ni_{26.89}O_{1.09}$ [15]. After the samples were annealed at 500 °C, drop of resistance was observed. The reduction of resistance is attributed to the growth of Cu crystals. At the as-deposited state, the sputtered Cu has small crystal size with relatively higher electrical resistivity. After the annealing, the Cu grain coarsening results in the decrease of overall electrical resistance. At 600 °C and 700 °C, a slight increase of resistance was observed. This could be an indication that a subtle change in the elemental profile and even interface reaction might have taken place. Detailed analysis will be discussed later. At 800 °C, the resistance increases drastically. Since Cu carries most of the electron flow, the change of resistance suggests that the catastrophic failure of Cu barrier occurs at 800 °C for both samples.

The phase evolution during the annealing is given by XRD in Fig. 2. For both samples, only Cu diffraction peaks were observed at temperatures up to 600 °C. It was noted that the full width at half maximum (FWHM) of Cu peaks were narrower at higher annealing temperatures, which supports the early explanation that Cu grain coarsening has resulted in the sheet resistance drop after annealing. At 700 °C, crystalline Ta_2O_5 phase (Fig. 2a) appeared in the $Cu/Ta_{67.34}Ni_{27.06}O_{5.60}/Si$ sample, and no other phases were detected. As will be discussed later, nano-sized Cu_3Si grains were found at the 700 °C-annealed $Cu/Ta_{73.25}Ni_{26.10}O_{0.65}/Si$ interface as observed in TEM. The Cu_3Si showed grain size of less than 10 nm, so it was not detected by XRD (Fig. 2b) when the amount is low. At 800 °C, several crystalline phases with sharp peaks were observed in both samples: $TaSi_2$ and Cu_3Si were found in the $Cu/Ta_{73.25}Ni_{26.10}O_{0.65}/Si$, and Ta_5Si_3 and Cu_3Si in $Cu/Ta_{67.34}Ni_{27.06}O_{5.60}/Si$ samples. Cu_3Si were observed in both samples, indicating complete failure of Cu diffusion barrier.

The films annealed at different temperatures were scanned under SIMS to examine the extent of inter-diffusion. As shown in Fig. 3, at the as-deposited state, there was a sharp transition in the depth profile of all elements, and the interfaces between neighboring layers are clearly identifiable. It is noted that in the $Cu/Ta_{67.34}Ni_{27.06}O_{5.60}/Si$ sample, significant amount of oxygen was detected in the barrier film layer, while in $Cu/Ta_{73.25}Ni_{26.10}O_{0.65}/Si$ sample, only a small O peak was observable at the barrier/Si interface, which is probably due to the presence of SiO_2 residue. Small amount of Cu diffusion into the Ta–Ni layers was observed for both samples after they were annealed at 600 °C for 30 min. There was no reaction between Cu and Si, and the boundary between neighboring layers was still clearly identifiable. At 700 °C, extensive Cu diffusion into the Si was clearly observed, but there was a difference between the $Ta_{67.34}Ni_{27.06}O_{5.60}$ and $Ta_{73.25}Ni_{26.10}O_{0.65}$ samples. In the sample with negligible oxygen content ($Ta_{73.25}Ni_{26.10}O_{0.65}$), Cu has diffused through to the Si side more severely (Fig. 3f) than in the $Ta_{67.34}Ni_{27.06}O_{5.60}$ sample (Fig. 3e). There was a peak of Cu accumulation at the Ta–Ni/Si interface, which is confirmed to be due to the Cu_3Si compound formation by TEM observation to be discussed later.

Fig. 4 shows the TEM pictures of the two samples after annealing at 600 °C, 700 °C and 800 °C. After 600 °C annealing, both samples showed clear interface between neighboring layers, and there was no interfacial reaction or self-crystallization. At 700 °C, small particles were observed at $Ta_{73.25}Ni_{26.10}O_{0.65}/Si$ interface (Fig. 4d). EDX indicates that these particles are composed of Cu and Si with atomic ratio close to 3:1. This correlates well with the early SIMS observation that Cu accumulates at the Ta–Ni/Si interface. Based on the atomic ratio as well as XRD results for annealed samples at higher temperatures, the particles formed should be Cu_3Si. On the other hand, no Cu–Si phase was formed at the Ta–Ni/Si interface in the $Ta_{67.34}Ni_{27.06}O_{5.60}$ sample. Instead, at the $Cu/Ta_{67.34}Ni_{27.06}O_{5.60}$ interface, newly formed grains were observed, which were identified as Ta oxide by EDX. The compounds are crystalline Ta_2O_5 based on XRD results (Fig. 2a). The comparison reveals the difference in barrier performance between the two samples. While for the oxygen-containing $Ta_{67.34}Ni_{27.06}O_{5.60}$ sample, there is no Cu–Si reaction probably because the Cu concentration has not reached the critical level needed for the compound formation at 700 °C. For the $Ta_{73.25}Ni_{26.10}O_{0.65}$ sample, Cu_3Si particles of less than 10 nm in size have started forming at 700 °C (Fig. 4d). Thus we can conclude that small amount of oxygen helps not only to stabilize the amorphous structure as we have reported before [15], but also to delay the Cu diffusion and Cu–Si compound formation, leading to improved barrier performance. At 800 °C, both films lost their integrity as shown by Fig. 4e and f where Cu and Ta–Ni layers were not distinguishable.

4. Conclusion

Ta–Ni amorphous thin films with 5.6 at% and 0.65 at% oxygen were formed by sputter deposition and evaluated for Cu diffusion barrier performance. The comparison between the two types of samples has revealed different barrier performance. While diffusion of Cu into Si was observed for both samples at 700 °C, formation of Cu_3Si only occurred in the oxygen-deficient $Ta_{73.25}Ni_{26.10}O_{0.65}$ sample, indicating that incorporation of a few percent of oxygen could effectively retard Cu diffusion and reaction with Si. The addition of oxygen into Ta-based thin film during sputtering deposition can be easily controlled via the application of a bias voltage. Our work has shown that amorphous Ta–Ni thin films are good candidates for Cu diffusion barrier for semiconductor device fabrication. It is further suggested incorporation of a small amount of oxygen could lead to enhanced barrier performance for Ta-based barrier films.

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