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The effect of oxygen in the annealing ambient on interfacial reactions of Cu/Ta/Si multilayers

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Abstract

Interfacial reactions of Cu/Ta/Si multilayers after thermal treatment were investigated using transmission electron microscopy. The Cu and Ta films were deposited onto Si wafer by ionized metal plasma technique. The samples were then annealed at 400, 500, 550 and 600°C in purified Ar atmosphere for 30 min. The effect of oxygen in the atmosphere on the thermal stability is studied. An interlayer of Ta oxide was observed between Cu and Ta after annealing at 400, 500 and 550°C. It is evident that oxygen as residual gas from furnace ambient can diffuse through Cu grain boundaries to form the Ta oxide layer. After annealing at 600°C, Si reacted with Ta to form $TaSi_2$ at the interface of Ta and Si, in the meantime Cu_3Si with surrounding SiO_2 formed in the Si substrate. The thermal stability of the Cu/Ta/Si samples was also examined in a two-step annealing treatment of 400°C for 30 min, followed by 600°C for 30 min. Even though interlayers of crystalline Ta–Cu oxide and Ta silicide were formed, Cu silicides were not observed. Formation of TaO_x interlayer at the first stage of 400°C annealing may inhibit Cu diffusion into the Si substrate in the second stage of the 600°C annealing process. © 2001 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Cu is the interconnected metal for the next generation ULSI devices because of its lower bulk resistivity [1] and higher electromigration resistance than Al [2]. However, Cu can easily react with Si at a temperature as low as 200°C [3] and diffuses fast in SiO_2 [4] under electrical field bias, resulting in degradation of device performance. Therefore, a diffusion barrier layer is needed to prevent Cu from Si and SiO_2. Tantalum is a promising material as a diffusion barrier for Cu metallization because Ta and Cu are mutually insoluble [5–12]. In addition, Ta has a relative low resistivity in the range of 100–130 $\mu\Omega\ cm^{-1}$. However, the thermal stability of Ta is an important issue for microelectronic fabrication due to its high reactivity with Si at high temperatures. The thermal stability of Ta barrier layer depends on thickness [5] and temperature. It was reported that 50-nm Ta prevents reaction of Cu with Si up to 600°C for 30 min in the purified He ambient [8]. When Cu penetration through the Ta barrier occurs η''-Cu_3Si phase and hexagonal-$TaSi_2$ layer are formed [6,8]. The thermal stability of the Ta barrier layer may also depend on the processing ambient. It was found that nitrogen ambient could improve the thermal stability of Ta up to 700°C [8]. The oxygen ambient enhances the diffusion of Si through the metal layer and formation of SiO_2 on the top of metal was observed in Si/metal structures [13]. Oxidation of $TaSi_2$/Si also shows similar enhanced diffusion behavior of Si [14]. It was, therefore, thought that oxygen might affect the

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behavior of interfacial reactions for the Cu/Ta/Si. The effect of oxygen in ambient for thermal processing for Cu/Ta/Si are seldom reported in the published literature that may be important for the following processing in ambient-containing oxygen. In this work, we have investigated the effect of oxygen residual from a vacuum furnace on the thermal stability of a 25-nm thick Ta barrier between Cu and Si substrate at various annealing temperatures. Field-emission transmission electron microscopy (TEM) with X-ray energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) mapping was used for the microstructural and compositional characterization.

2. Experimental

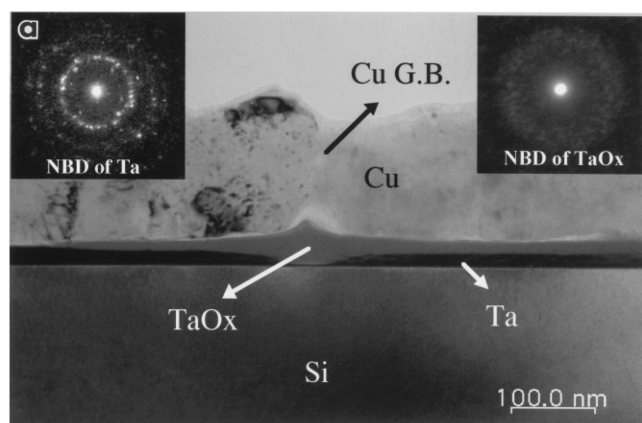
The Cu and Ta films were deposited on 8-inch silicon wafers in an Applied Materials Electra™ system that utilized ionized metal plasma (IMP) processing technology [15]. The base pressure of the IMP chambers was typically $\sim 10^{-8}$ torr. The stacking sequences and thickness of the deposited films were Cu (150 nm)/Ta (25 nm) on Si wafers.

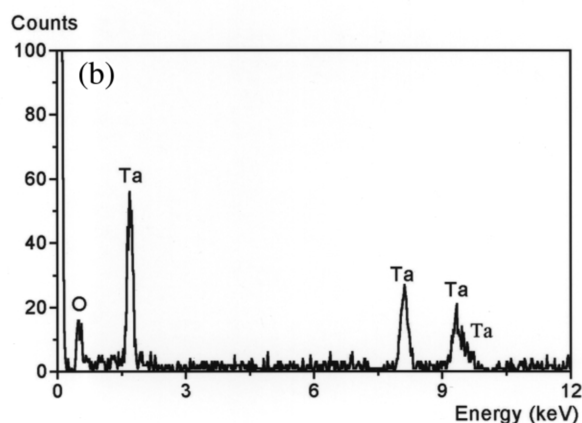
The vacuum furnace using silica tube heated by SiC heating elements was evacuated with a rotary blower pump. Before feeding with Ar gas, the furnace was purged several times with Ar and pumped down to 10^{-2} torr range. All samples were treated in the furnace at 400, 500, 550 and 600°C annealing processes in purified Ar (4 N) atmosphere with a pressure of 3 mtorr. The partial pressure of oxygen was estimated to be approximately 10^{-3}–10^{-4} torr in our experimental conditions from the result of a leakage test. A two-step 400–600°C process was also performed. All samples were cut into 1×1 cm^2, before being put into the furnace. Annealing time at each temperature was 30 min. Wedge method [16] for grinding and polishing was used for cross-sectional TEM specimen preparation. The final step was ion milling to perforation. Mo grids instead of Cu ones were used to mount TEM specimens to obtain clean Cu EDS signals from the Cu film in the samples. A JEOL 2010F field emission TEM, equipped with an EDS spectrometer and a Gatan energy filter was used for studying the structures and chemical compositions. Analysis of electron energy loss spectroscopy (EELS) was performed with the Gatan energy filter.

3. Results and discussion

The microstructure of Cu/Ta/Si films in the as-deposited sample has no interlayer between the films as observed from cross-sectional high-resolution images. The structure of the as-deposited Ta layer is a nanocrystalline beta phase. No texture or preferred orientation of Ta grains can be observed with Si substrate. After 500°C anneal, the typical microstructure of a Cu/Ta/Si sample is shown in Fig. 1a. A 6–20-nm thick interlayer between Cu and Ta layers is clearly observed with uniform gray contrast. A nanobeam diffraction pattern in the inset of Fig. 1a shows that the interlayer is amorphous. The EDS spectrum in Fig. 1b obtained by using a nano-size electron beam indicates that the interlayer contains Ta and O elements. The inverted V shape of the amorphous Ta oxide layer suggests that oxygen from ambient atmosphere may diffuse along grain boundaries of Cu and gradually oxidize Ta. An oxygen elemental map in Fig. 1c (*K*-edge 532 eV, energy window width 30 eV) obtained by the Gatan energy filter clearly shows the oxygen distribution along a Cu grain boundary. This result is similar to our previous result from Cu/Ta/SiO_2/Si structure after annealing at the same temperature in Ar atmosphere in which Ta oxide formed between Ta and Cu [17]. It is noted that the Ta layer remains to be beta phase after 500°C/30 min annealing as the diffraction pattern in Fig. 1a inset shows. Fig. 2a reveals a triangular region of light contrast in the silicon substrate beneath the barrier layer from a sample annealed at 550°C. Lattice imaging and nano-diffraction patterns show that it is just pure Si. EDS spectra in Fig. 2b compare the Si peak intensities at 1.74 keV (in net counts) from the triangular region with those from the adjacent areas in the Si substrate. Depletion of Si mass is, therefore, evident in the triangular region. As a result, Si atoms reacted with the Ta at this temperature to form an amorphous Ta silicide layer, which exhibits dark contrast in 2–5-nm thick between Ta and Si in Fig. 2a. The amorphous Ta silicide has been confirmed by both EELS and EDS spectra which show only Ta and Si signals from the layer in Fig. 2c,d. Formation of amorphous Ta silicide between Ta and Si at 550°C has been reported [18]. Outdiffusion of Si into Ta is generally found for formation of Ta silicide [19]. Interestingly, it is found that most of the triangular regions are located around Ta/Ta oxide boundaries roughly below the Cu grain boundaries where Ta oxide also began to form and is thicker than the rest of the areas. It is most likely that the oxidation of Ta might enhance the Si and/or vacancies migration and Si diffusing along Ta/Si interface to form Ta silicide. In this treatment, no Cu penetration through the TaO_x and Ta films into Si substrate occurred. In addition, EELS data reveals that some Si were dissolved in Ta.

Fig. 3a shows the microstructure of a sample after 600°C annealing. A reacted phase surrounded by the amorphous layer was found in the Si substrate. The reacted phase is η''-Cu_3Si, which has long period structure as analyzed from diffraction patterns and the surrounding amorphous layer, is identified to be SiO_2 by EELS analysis. No metallic Ta and Ta oxide layers were found, instead a 50-nm thick layer of $TaSi_2$ was





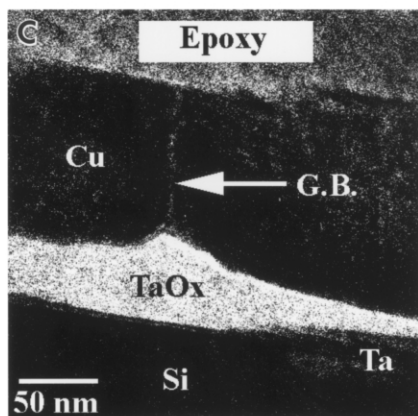


Fig. 1. (a) Cross-sectional TEM image after 500°C annealing for 30 min. (b) EDS spectrum of the interlayer between Cu and Ta layers. (c) Oxygen map from energy filter.

formed on top of the sample surface as shown in Fig. 3a,b. Previous works [6,8] reported similar results for copper silicide formation after treated at room temperature.

It is well known that Ta and Cu are mutually insoluble [20]. Grain boundary diffusion is probably the path for Cu passing through Ta. Using the diffusion constant of Cu in Ta [8], the diffusion distance is estimated to be 6 nm for 30 min at 600°C. Therefore, Cu motion in Ta is quite slow in the temperature range of 400–700°C. For a 25-nm Ta layer as used in this work, Cu penetration may not be the only reason to cause the failure. Ta silicide formation as a result of outdiffusion of Si may also have a role. Before oxygen diffusion to reach Ta at 600°C, Cu inward diffusion could occur while Si outward diffusion started. Vacancies left in the Si depleted regions could provide a strong driving force for Cu to accelerate into Si to form Cu_3Si. In the mean while, Ta silicide with the presence of Cu would crystallize as $TaSi_2$.

In the present study, we believe that mutual diffusion of the four major elements Cu, Ta, Si and O with interfacial reactions among them may occur at 600°C. At 550°C oxygen from ambient diffuses through grain boundaries of Cu to the Cu/Ta interface at which Ta oxide forms. Once the oxide layer has formed, it may retard diffusion of Cu through Ta layer. Hence, it is apparent that oxygen diffusion is faster than Cu penetration into Ta and Si outdiffusion. However, oxygen at 600°C is associated only with SiO_2 which is the product of oxidation of either Cu_3Si or $TaSi_2$ SiO_2 has been shown to be more stable than Ta oxide [21]. It may explain why Ta oxide is not seen after 600°C annealing.

It has been found that Cu penetration precedes and promotes Ta silicide formation [8]. They have reported that the formation temperature of $TaSi_2$ phase could be decreased with the presence of Cu [6]. Therefore, with sufficient supply of Si at this temperature, reaction of Si with Ta to form hexagonal-$TaSi_2$ phase at 600°C may be possible in our case. Further evidence is shown in our previous work on the thermal stability of $Cu/Ta/SiO_2/Si$ [17]. It shows that without free silicon supply, amorphous Ta oxide can be stable at 600°C. No Ta–Si–O ternary compound has been predicted from thermodynamic calculation of phase diagram [22]. Furthermore, an oxidation experiment of $TaSi_2/Si$ has shown that the SiO_2 layer formed in dry oxygen ambient has the thickness of approximately 7 nm [14]. Also from a previous report [23], at equilibrium, the reaction of Ta oxide with silicon may produce $TaSi_2$ or metallic Ta and SiO_2. The theoretical phase diagram indicates that $TaSi_2$ can coexist with SiO_2, but not with Ta oxide [22]. Therefore, $TaSi_2$ formation could be more favorable than Ta oxidation at 600°C, while Ta oxide formed at 550°C is thought to be possible because $TaSi_2$ formation has not occurred.

Reaction of Si with Cu to form η''-Cu_3Si phase has been shown to take place at low temperature of approximately 200°C. The η''-Cu_3Si phase contains either high density of stacking faults or vacancies [24]. It has been reported [25,26] that the η''-Cu_3Si may catalyze the oxidation of Si due to its high density of defects. Oxygen can also diffuse through the reacted layer and then along the interface of Cu_3Si/Si to form silicon dioxide layer. An oxygen elemental map in Fig. 3c

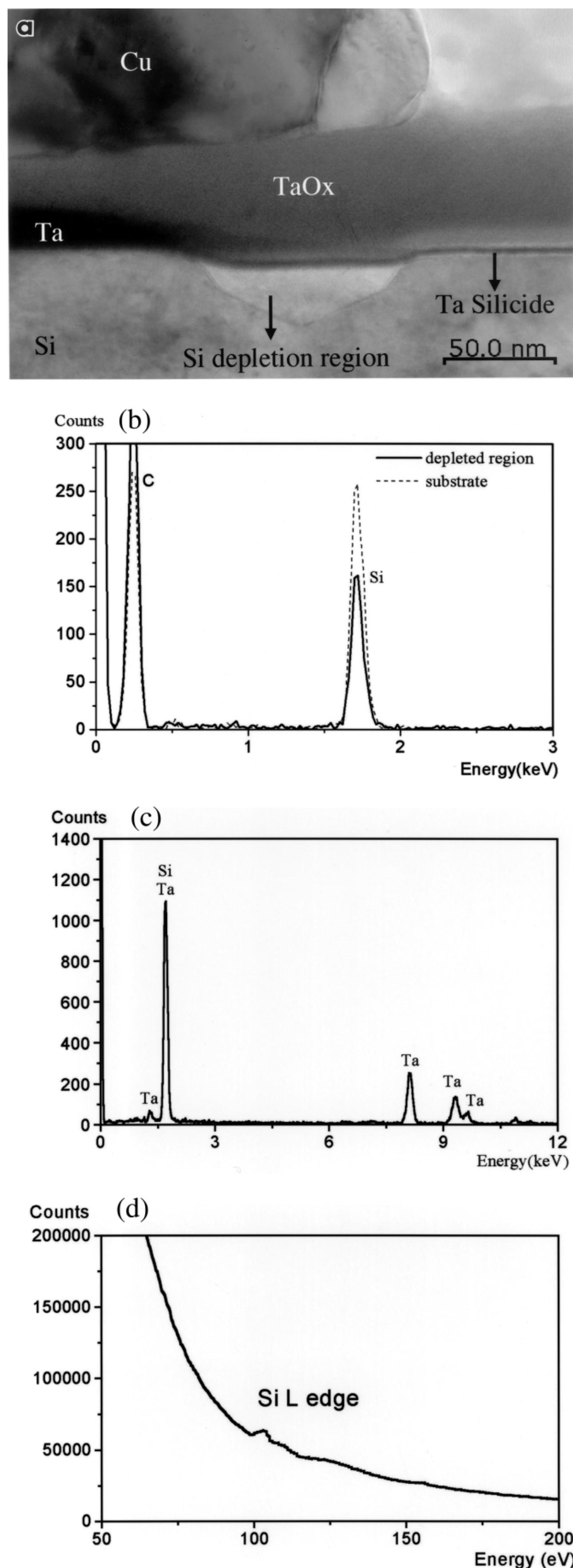


Fig. 2.

shows formation of oxide at the interface between Si and Cu_3Si that the catalyzing process starts, oxidation of Cu_3Si will produce SiO_2 and release free Cu to form new Cu_3Si. The process will continuously repeat itself until all the Cu is consumed. It is, therefore, believed that formation of η''-Cu_3Si may promote penetration of Cu through the reacted barrier layer into Si substrate for further growth of Cu silicide. As Cu_3Si is easily oxidized, it may absorb most of oxygen in the form of SiO_2, so that $TaSi_2$ is prevented from being oxidized. It has been suggested that Cu could diffuse along grain boundaries in Ta films until it reaches the Si, then rapidly migrate along the Ta/Si interface where Cu_3Si nucleation sites are encountered [8,12]. Recently, we have found some Cu_3Si precipitates in such depleted regions in another study of thermal stability of Ta_2N barrier between Cu and Si [27]. Hence, we speculate that the interface between the depleted regions and the barrier layer could be the nucleation sites for Cu_3Si. Further experiments will confirm this argument.

In order to realize the effect of Cu diffusion with interfacial behavior of Ta/Si interface on thermal stability, a two-step annealing treatment was carried out. The treatment consisted of 400°C/30 min annealing, followed by a 600°C/30 min one. From the 400°C annealing result, a layer of Ta oxide in 4–6-nm thickness as shown in Fig. 4a was formed between Cu and Ta due to the strong oxygen affinity of Ta. We expect that TaO_x layer could be acted as a strong diffusion barrier against Cu penetration, even though its resistance may be high for device performance. If the oxide could really inhibit the Cu motion, it is feasible to investigate the interfacial reaction between Ta and Si without Cu interference. Fig. 4b shows a cross-sectional TEM image after the two-step annealing. The microstructure is surprisingly different from that in the sample only treated with 600°C annealing. First, no copper silicide can be observed, indicating that Cu has not penetrated into Si. Secondly, although there is still an interlayer approximately 4–6-nm thick between the Cu and Ta layers, the lattice fringes indicate it is a crystalline phase rather than amorphous TaO_x. From EDS and NBD analyses in Fig. 4c,d, the composition of the interlayer consists of Cu, Ta and O and structure has d-spacings in 0.61 and 0.11 nm close to the result of $Cu/Ta/SiO_2/Si$ multilayers after 600°C in a low-vacuum condition [17]. The crystalline Ta–Cu oxide layer between Cu and Ta appears to be almost per-

Fig. 2. (a) Cross-sectional TEM image after 550°C annealing for 30 min. (b) The EDS spectra obtained from depleted area and the adjacent Si substrate. (c) EDS spectrum obtained from Ta silicide indexed in Fig. 2a. (d) EELS spectrum obtained from Ta Silicide indexed in Fig. 2a.

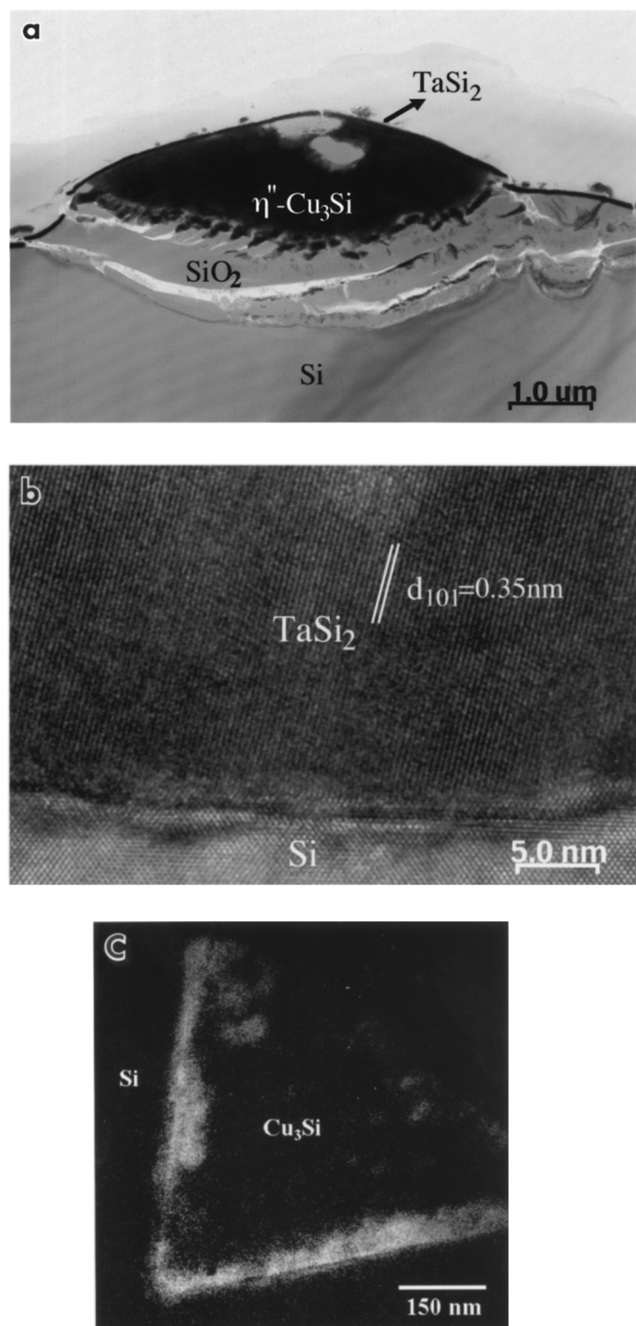


Fig. 3. (a) Cross-sectional TEM image after 600°C annealing for 30 min. (b) High-resolution TEM image obtained from Ta barrier. (c) Oxygen elemental map of a Cu_3Si from another area.

fectly oriented with long axis perpendicular to the interface. With few grain boundaries observed in the Ta–Cu oxide layer, it could effectively inhibit the Cu diffusion. The thickness of the oxide did not increase in the second stage of annealing at 600°C, implying no further oxidation. The thickness of Ta oxide is also thinner than that in $Cu/Ta/SiO_2$ sample treated at the same temperature. In addition, the image contrast shows that there are two layers between the Ta–Cu oxide and Si substrate. The upper layer with darker contrast is the original Ta whose thickness has been reduced to approximately 17 nm. The gray zone above Si substrate with thickness of approximately 12–17 nm is identified to be a Ta_5Si_3 phase as the high-resolution image at Ta/Si interface in Fig. 4e shows. This is in consistence with a previous report that Ta-rich silicide can form at 600°C without the presence of Cu [28]. In general, if the Si is the diffusion species, the metal-rich silicide phase forms first. In the $Cu/Ta/SiO_2$ sample, there is no free silicon supply at 600°C, so that silicide formation is unlikely. Formation of Ta-rich phase Ta_5Si_3 is reported to be possible at 630°C for 1 h, while a silicon-rich phase $TaSi_2$ forms at higher temperature approximately 700°C for 1 h [28]. Ta_5Si_3 may be transformed to $TaSi_2$ with the Cu presence in an early stage of annealing.

In the two-stage annealing, the unreacted Ta shows reaction of Ta with Si at 600°C without Cu is slow, in contrast with the fact that all Ta are in the form of $TaSi_2$ when Cu is present. The remaining 17-nm thick Ta reduced from the initial 25-nm thickness, demonstrating that 8-nm thick Ta has consumed for Ta_5Si_3 formation. Therefore, it is likely that Si outdiffusion to Ta can reach at least 8-nm distance after 30 min. For the case of the single stage annealing at 600°C, if Cu could penetrate Ta without oxide in the way, it would have traveled approximately 6 nm according to the calculated diffusion distance. There should have been Ta left if no other mechanism was in operation for Cu and Si reaching each other. Though the mechanism is not actually known as the evidence is insufficient, we suspect that, as mentioned before, vacancies in the Si substrate might be the cause for accelerating Cu penetration. Nevertheless, we are unable to explain the action of oxygen, which should diffuse faster than Cu to Ta and Si and why no Ta oxide forms and all oxygen form SiO_2.

In the single stage of annealing at 550, Ta oxide can block Cu penetration, while at 600°C the absence of oxide allows Si react with Cu and Ta to form Cu_3Si and $TaSi_2$, so that the barrier stability was destroyed. For the two-stage annealing, the amorphous Ta oxide layer forms at the first stage, which crystallizes as Ta–Cu oxide after reacting with Cu at 600°C. If Ta–Cu oxide is stable, Cu has little chance to directly react with silicon to form copper silicide in the second stage annealing. Based on the above observations, it can be concluded that residual gas of oxygen in Ar furnace ambient has a significant effect on the thermal stability of Ta barrier between Cu and Si.

4. Conclusions

The thermal stability of Ta barrier layer in Ar atmosphere at various temperatures is summarized as fol-

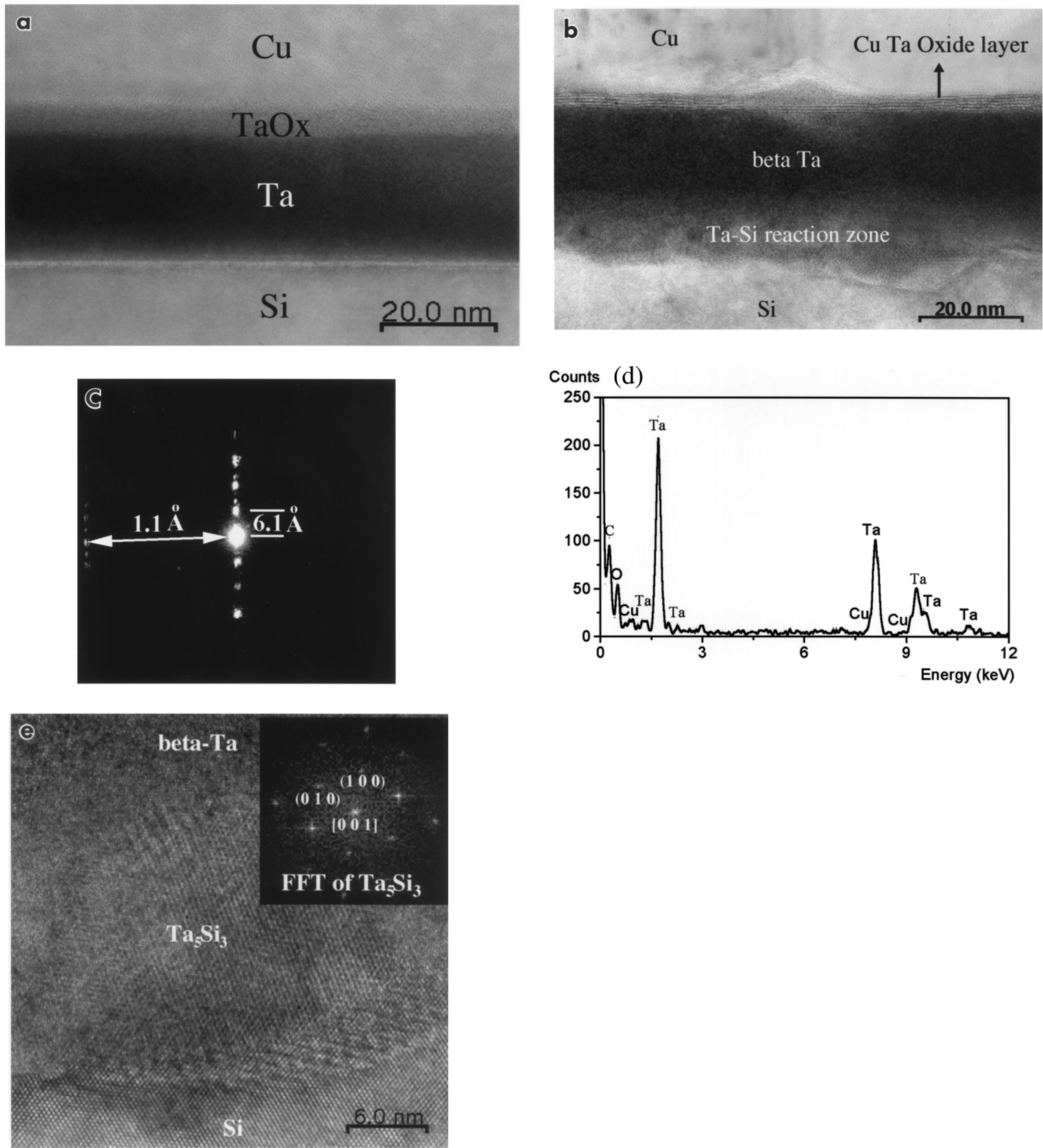


Fig. 4. (a) Cross-sectional TEM image after 400°C first step annealing. (b) Cross-sectional TEM image after the two-step annealing (400–600°C). (c) Nano-beam diffraction obtained from the interlayer between Cu and Ta layer. (d) EDS spectrum of interlayer between Cu and Ta layers. (e) High-resolution TEM image obtained from the interface of Ta layer and Si substrate.

lows. At 500°C, oxygen as residual gas from furnace ambient can diffuse through Cu grain boundaries to Ta and form TaO_x layer between Cu and Ta due to the strong oxygen affinity of Ta. At 550°C, the out-diffusion of silicon becomes noticeable, resulting in a depleted region in Si substrate and formation of amorphous Ta silicide. No Cu silicide formed for samples annealed at 500 and 550°C. After 600°C annealing, the silicidation of Ta as $TaSi_2$ and formation of copper silicide with SiO_2 were observed. No Ta oxide can be seen. For a two-step annealing at 400°C/30 min followed by 600°C/30 min, the initially formed TaO_x layer transformed into a crystalline Ta–Cu oxide in 4–6-nm thick which effectively inhibits Cu diffusion. Therefore, Cu is

prevented from directly reacting with Si to form Cu_3Si. Meanwhile, the Ta layer reacted with Si to form Ta_5Si_3.

References

[1] H. Takasago, K. Adachi, M. Takada, J. Electron. Mater. 18 (1989) 319.
[2] J.R. Lloyd, J.J. Clement, Thin Solid Films 262 (1995) 135.
[3] E.R. Weber, Properties of Silicon, The Instituation of Electrical Engineers, London, 1985.
[4] J.D. McBrayer, R.M. Swanson, T.W. Sigmon, J. Electrochem. Soc. 133 (1986) 1242.
[5] M.T. Wang, Y.C. Lin, M.C. Chen, J. Electrochem. Soc. 145 (1998) 2538.
[6] K. Holloway, P.M. Fryer, Appl. Phys. Lett. 57 (1990) 1736.
[7] E. Kolawa, J.S. Chen, J.S. Reid, P.J. Pokela, M.-A. Nicolet, J. Appl. Phys. 70 (1991) 1369.
[8] K. Holloway, P.M. Fryer, C. Cabral Jr., J.M.E. Harper, P.J. Bailey, K.H. Kelleher, J. Appl. Phys. 71 (1992) 5433.
[9] P. Catania, J.P. Doyle, J.J. Cuomo, J. Vac. Sci. Technol. A10 (1992) 3318.
[10] H. Ono, T. Nakano, T. Ohta, Appl. Phys. Lett. 64 (1994) 151.
[11] M. Stavrev, C. Wenzel, A. Möller, K. Drescher, Applied Surface Science 91 (1995) 257.
[12] J.S. Kwak, H.K. Baik, J.–H. Kim, S.-M. Lee, Appl. Phys. Lett. 71 (1997) 2451.
[13] D. Gupta, ed., Diffusion Phenomena in Thin Films (Park Ridge, N.J., U.S.A., Noyes Publication 1988), p. 323.
[14] S.P. Muraka, D.B. Fraser, W.S. Lindenberger, A.K. Sinha, J. Appl. Phys. 51 (1980) 3241.
[15] G.A. Dixit, W.Y. Hsu, A.J. Konecni, S. Kirshnan, J.D. Luttrner, R.H. Havemann, J. Forster, G. D. Yao, M. Narasimhan, Z. Xu, S. Ramaswami, F.S. Chen, J. Nulman, IEEE IEDM Tech. Dig. (1996) 357.
[16] H. Zhang, Thin Solid Films 320 (1998) 77.
[17] K.-M. Yin, L. Chang, F.-R. Chen, J.J. Kai (Unpublished work).
[18] J.Y. Cheng, L.J. Chen, J. Appl. Phys. 69 (1990) 2161.
[19] H.L. Meyerheim, B. Lengeler, H.E. Goel, J. Appl. Phys. 68 (1990) 2694.
[20] T.B. Massalski, ed., Binary Alloy Phase Diagram, (American Society for Metals, Metals, Park, OH, 1986), Vol. 1, p. 960.
[21] R. Beyers, R. Sinclair, M.E. Thomas, J. Vac. Sci. Technol. B2 (1984) 781.
[22] R. Beyers, J. Appl. Phys. 56 (1984) 147.
[23] K.C. Saraswat, R.S. Nowicki, J.F. Moulder, Appl. Phys. Lett. 41 (1982) 1127.
[24] J.K. Solberg, Acta Cryst. A34 (1978) 684.
[25] C.S. Liu, L.J. Chen, J. Appl. Phys 74 (9) (1993) 5501.
[26] L. Stolt, A. Charai, F.M. D'Heurle, P.M. Fryer, J.M.E. Harper, J. Vac. Sci. Technol. A9 (1991) 1501.
[27] K.-M. Yin, L. Chang, F.-R. Chen, J.J. Kai (Unpublished work).
[28] A.N. Noya, M. Takeyama, K. Sasaki, E. Aoyagi, K. Hiraga, J. Vac. Sci. Technol. A15 (1997) 253.