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Author(s)	Li, S.; Dong, Zhi Li.; Maung Latt, K.; Park, H. S.; White, T.
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Formation of Cu diffusion channels in Ta layer of a Cu/Ta/SiO₂/Si structure

S. Li,^{a)} Z. L. Dong, K. Maung Latt, and H. S. Park

School of Materials Engineering, Nanyang Technological University, Singapore 639798, Singapore

T. White

Environmental Technology Institute, Singapore 637723, Singapore

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Three mechanisms for the formation of Cu diffusion channels in the Ta layer of a Cu/Ta/SiO₂/Si structure are proposed. First, it is suggested that stacking faults formed during the recovery process induce localized regions of high internal energy in the Ta layer, from which Cu channels originate. Second, chemical reaction occurs at 800 °C and forms Ta₄CuO₁₁ across the Cu/Ta interface in Cu and Ta layers, which opens up channels for Cu diffusion. Third, triple junctions at the grain boundary of the Cu and Cu/Ta interface provide sites for the initiation of channel formation at 800 °C. At 950 °C, these channels in the diffusion barrier are absent, but Ta was oxidized into disordered Ta₂O₅ that may contain pathways for Cu diffusion. © 2002 American Institute of Physics. [DOI: 10.1063/1.1465107]

Copper is a promising material for ultralarge scale integration devices because of its superior electrical resistivity and resistance to electromigration.^{1–3} However, the diffusivity of Cu in SiO₂ and Si is very intense^{4,5} and will result in deep-level trapping which seriously degrades the electronic properties of silicon devices.^{6–8} A Ta layer is widely used as a diffusion barrier because of its high thermal stability and limited solid solubility with Cu.^{9–11} Although its chemical stability and durability in a Cu/Ta/SiO₂/Si structure at high processing temperature have been investigated,^{12–14} the formation of Cu diffusion channels in the diffusion barrier is not clearly understood. In the present work, analytical scanning transmission electron microscope (STEM) and energy dispersive spectrometry (EDS) were employed to probe the mechanistic aspects of the Cu diffusion.

A 250 nm thick SiO₂ layer was deposited on a Si substrate using plasma enhanced chemical vapor deposition (PECVD). Subsequently, 30 nm Ta and 200 nm Cu layers were deposited by the ionized metal plasma (IMP) deposition technique without breaking vacuum. The as-deposited samples were divided into three groups and annealed at 650, 800, and 950 °C, respectively. The interfaces, microstructure and elemental distribution in the Cu/Ta/SiO₂/Si structure were characterized by STEM, while x-ray diffraction (XRD) was used to identify the products of chemical reactions. A standard four-point method was employed to measure the sheet resistance (R_s), which showed a slight increase from 0.12 to 0.15 Ω/cm² over the annealing temperature range of 350–650 °C but then abruptly increased to 0.81 and 0.88 Ω/cm² at 750 and 800 °C, respectively. However, further annealing at 900 and 950 °C reduced R_s to 0.13 and 0.16 Ω/cm², as shown in Fig. 1.

In the as-deposited sample, polycrystalline β-Ta and Cu were distributed in the Ta and Cu layers. An amorphous interlayer 4 nm thick was observed, however, its mechanism of formation is not clear although it was reported that a TaO_x

interlayer can form by oxygenation.¹⁴ Definitive analysis of such an interlayer is difficult due to electron beam spreading.

After annealing at 650 °C for 30 min, the Ta layer contained stacking faults directly beneath the Cu/Ta interface (Fig. 2). This area consisted of two distinct regions, marked A and B. Region A was ~50×20 nm² in extent and contained a higher density of stacking faults than the somewhat smaller region B (~50×10 nm²). The (001) plane of the Ta crystal was parallel to the Cu/Ta interface (see the inset in Fig. 2). The stacking fault period was ~3 nm and the grain boundary exhibited a feather feature (shown by arrows). The formation of faults is attributable to the recovery of the strained crystal. It has been reported that the as-deposited β-Ta thin film will be subjected to tensile strain parallel to the interface.¹⁵ Since the annealing temperature was much lower than the recrystallization temperature, which is 0.4 of the melting temperature of Ta (3020 °C), dislocations in the strained crystal can slip and rearrange in the sliding planes. Consequently, some sign dislocations pile up and form stacking faults of high internal energy. However, only some crystals with favorable orientations were subject to the maximum plane tensile stress on the dislocation-sliding plane, and relaxed into stacking faults. This recovery process may also occur in the early stage of annealing at 800 °C.

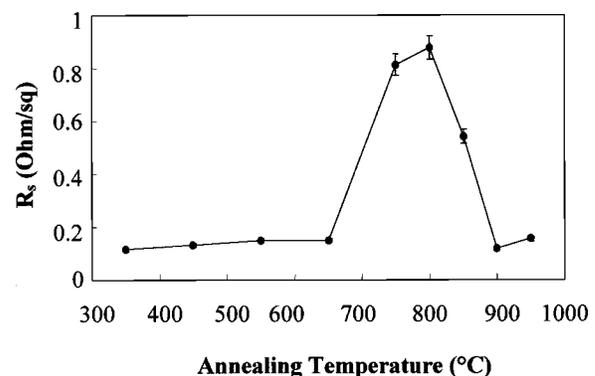


FIG. 1. Annealing temperature dependence of the sheet resistance of the samples.

^{a)}Author to whom correspondence should be addressed; electronic mail: assxli@ntu.edu.sg

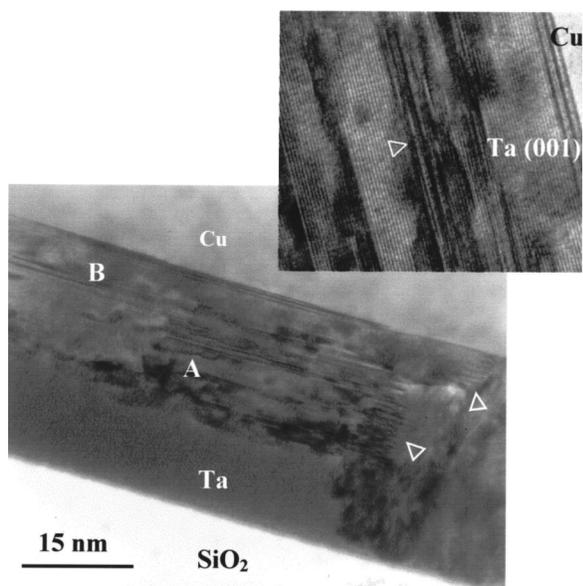


FIG. 2. TEM morphology of the Ta layer in the sample annealed at 650 °C for 30 min and high-resolution TEM image of the same area showing that (001) stacking faults formed in the Ta layer underneath the Cu/Ta interface (inset).

After annealing at 800 °C for 30 min, a ladle-shaped transparent area formed in the Ta layer; it had a handle ~13 nm thick and a total length of ~100 nm [Fig. 3(a)]. The ladle consisted of two regions, marked A and B. The sizes of regions A and B were similar to corresponding areas in Fig. 2 which contained a high density of stacking faults, implying that the microstructural change in the Ta layer occurred in the high energy area. EDS analysis indicated that the transparent area was Cu rich. The difference in contrast between regions A and B is interpreted as being due to different orientations of adjacent Cu crystals formed in areas with different densities of stacking faults. It is believed that Cu protuberantly migrated into the higher internal energy area of the Ta layer and formed the arc part of the ladle-shaped area, thus minimizing the energy of the system. Further growth and migration of Cu in the ladle-shaped area broke the diffusion barrier and formed an opening in the channel of the Ta layer [Fig. 3(b)]. Once the diffusion barrier was broken, Cu could easily migrate into the SiO₂. Elemental mapping shown evidence of Cu accumulated in the SiO₂ layer underneath the Ta layer, whereas the Ta layer was broken. However, the interface between the protruding area in the ladle-shaped Cu and Ta layer was distinct [Fig. 3(c)], indicating that no reaction occurred between Ta and Cu in this manner of channel formation.

It was observed that the reaction product Ta₄CuO₁₁, having an extent of ~250×150 nm², formed in the Ta layer that protruded toward the Cu layer [Fig. 3(d)]. Gaps between the compound and the Ta layer (shown by arrow) provide another channel in the Ta layer for the Cu diffusion. The chemical reactions among Cu, Ta, and O might also have initiated at areas with a large number of atomic-scale structural defects.

The diffusion barrier of the Ta layer was also broken in a triple junction of the grain boundary of the Cu and Cu/Ta interface [Fig. 3(e)]. It is believed that (1) the triple junction had higher energy and (2) the Cu atoms quickly diffused and

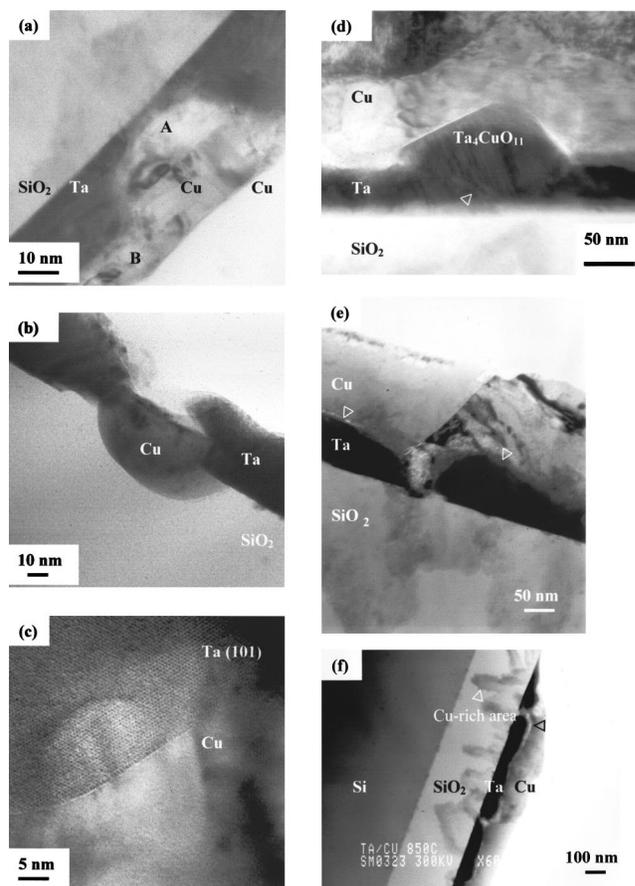


FIG. 3. (a) TEM morphology of the sample annealed at 800 °C for 30 min showing that the change in microstructure occurred in the Ta layer. (b) TEM morphology showing that an opening in the channel formed in the Ta layer and Cu subsequently, migrated into SiO₂ in a protuberant manner. (c) High-resolution TEM image showing that no reaction occurred between Ta and Cu in the manner of channel formation. (d) TEM morphology showing a Ta₄CuO₁₁ compound that formed in the Ta layer protruding toward the Cu layer where there are gaps between the compound and the Ta layer (shown by arrows). (e) TEM morphology showing that the diffusion channel that formed in a triple junction of the Cu grain boundary and the Cu/Ta interface in the sample annealed at 800 °C. (f) Scanning TEM morphology showing that Cu diffused into SiO₂ radially and quickly after the diffusion barrier was broken in the sample annealed at 800 °C.

gathered at the triple junction along the grain boundary and interface. The concentration of Cu in the triple junction caused an abrupt change in chemical potential between the triple junction and the Ta layer. This potential drove intense diffusion of Cu into the Ta layer and formed protrusive nucleation around the triple junction. Once nucleation was initiated in the Ta layer, Cu atoms diffused easily along the interface and boundary to replenish the loss of Cu in the triple junction. Simultaneously, Ta atoms diffused laterally along the interface and piled up around the junction (shown by arrows). This process also opens up another channel for Cu diffusion.

After the diffusion barrier was broken, Cu rapidly migrated into the SiO₂ radially [Fig. 3(f)] and evidence of this was seen by the elemental distribution in the structure mapped with EDS. The intense diffusion of Cu into the SiO₂ layer caused the resistivity to increase dramatically because of consumption of the Cu layer. The bright stripes along the Cu/Ta interface beside the channel (shown by arrow) may be due to the loss of Cu that replenished the Cu growth in the Ta layer.

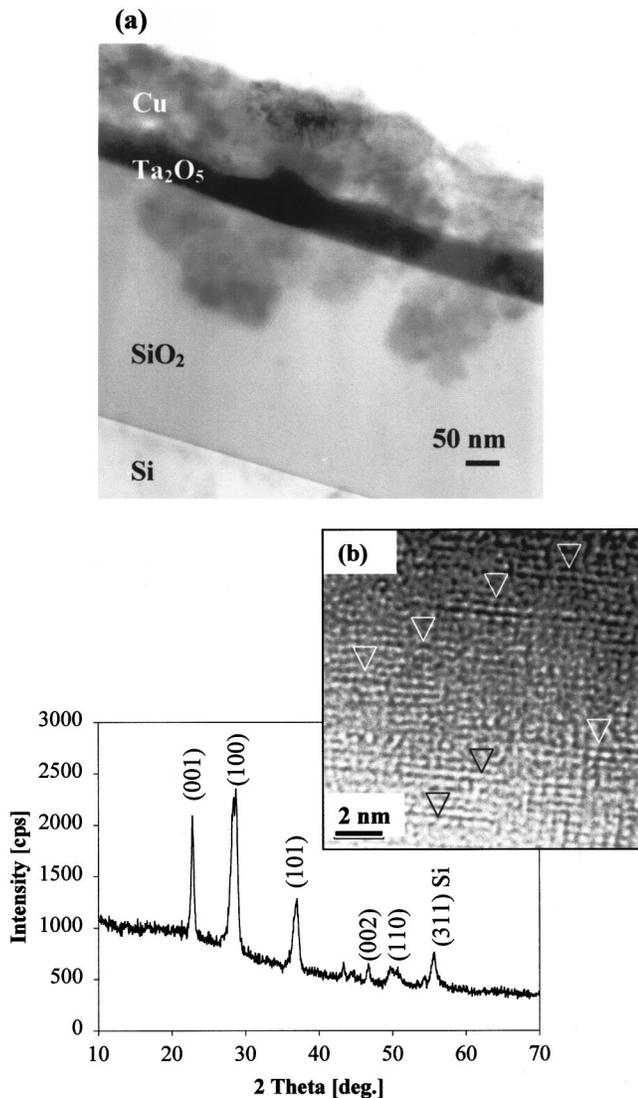


FIG. 4. (a) TEM morphology showing that no opening in the diffusion channel formed in the region of the original Ta layer. (b) XRD spectrum showing that the Ta layer was oxygenated into Ta_2O_5 . High-resolution image showing that the disordered Ta_2O_5 layer contained a number of (0001) stacking faults with mean periods of 1.55 nm (inset).

After annealing at 950 °C for 30 min, no diffusion channel was observed in the Ta layer [Fig. 4(a)]. Rather, lattice fringe images consistent with a hexagonal Ta_2O_5 (0001) plane show the region is oxidized; the formation of Ta_2O_5 can also be identified by XRD [Fig. 4(b)], which was carried from 10° to 70° (2θ) to exclude the high intensity Cu (220) peaks. The Ta_2O_5 was nonstoichiometric, as seen by (0001) stacking faults (arrows) with a mean period of ~ 2 nm. The stacking faults caused the (0001) d spacing to increase to 0.26 nm, and it may consist of a number of continuous array voids that can act as paths for Cu diffusion. In this case, only a little Cu penetrated through the Ta_2O_5 layer to the SiO_2

layer along the path of diffusion vertical to the interface and formed Cu_xSi_y . It is believed that Ta_2O_5 was more stable than β -Ta at high temperature. Therefore, Cu was not able to intrude into the diffusion barrier protuberantly as annealed at 800 °C, resulting in slightly higher resistivity than the as-deposited sample but much lower than the sample annealed at 800 °C.

In conclusion, it was found that there were three mechanisms of diffusion channel formation for Cu in the Ta layer of a Cu/Ta/ SiO_2 /Si structure. (1) Stacking faults that formed in the strained Ta layer after annealing at 650 °C or in the early stage of the annealing at 800 °C induced areas of high internal energy in the Ta layer. Minimization of the energy was achieved by Cu diffusing protuberantly into Ta in the high temperature process that ruptured the diffusion barrier. (2) The compound $\text{Ta}_4\text{CuO}_{11}$ formed across the Cu/Ta interface in the Cu and Ta layers at 800 °C, opening a channel for Cu diffusion. (3) Cu atoms accumulated at the triple junctions of the Cu grain boundary and the Cu/Ta interface through diffusion along the grain boundary and interface, causing an abrupt change in the chemical potential gradient. Consequently, Cu rapidly diffused into the Ta layer, forming protrusive nucleation and that perforated the diffusion barrier. However, the sample annealed at 950 °C showed no diffusion channel but, rather, formed nonstoichiometric Ta_2O_5 in the original diffusion barrier. It was found that there were a number of (0001) stacking faults formed by the continuing array of voids in Ta_2O_5 , which were the path of Cu diffusion across the diffusion barrier. Therefore, minimization of stacking faults in the strained Ta layer should reduce the possibility of Cu diffusion channel formation.

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