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# Interfacial reactions and failure mechanism of Cu/Ta/$SiO_2$/Si multilayer structure in thermal annealing

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## Abstract

The integrity of Cu/Ta/$SiO_2$/Si multilayer structure under nitrogen thermal annealing has been examined by sheet resistance measurement, X-ray diffraction, scanning electron microscopy, secondary ion mass spectroscopy, Rutherford backscattering spectrometry and cross-section transmission electron microscopy analysis. According to electrical measurement it was found that Ta diffusion barrier could preserve the integrity of the Cu/Ta/$SiO_2$/Si structure up to 650 °C in $N_2$ for 35 min. There are two causes by which the Cu/Ta/$SiO_2$/Si structure became degraded. One is the out diffusion Ta atoms towards the Cu film. The other factor is the formation of Cu, Ta and Cu–Ta oxide. Hence, Cu penetration is not the only reason to cause the failure; oxidation, phase transformation and interfacial reactions are also associated problems during thermal annealing.

*Keywords:* Tantalum (Ta); Interfacial reaction; Diffusion barrier; Metallization; Phase transformation

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## 1. Introduction

Copper is expected to come into widespread use as an interconnecting metal line in micro-electronic device and packaging applications. The demand for increasing a circuit performance, while downscaling the interconnect size to allow an increased circuit density, is placing huge demands on interconnect performance and reliability. Copper has been strongly considered as an interconnection material substitute for Al metallization because of its lower resistivity and higher electromigration resistance than Al and Al alloys [1]. However Cu diffuses easily into the interlayer dielectrics and device regions in silicon substrate, then reacts with Si atoms to form $Cu_3Si$ compounds at very low temperature ( ≈ 200 °C) [2], resulting in degradation of a circuit performance. Therefore, a barrier layer is essential to prevent Cu diffusion. In order to find a suitable diffusion barrier, a significant amount of research work has been performed and various diffusion barriers, including refractory metal (Ta and W) [3,4], nitrides (TiN and TaN) [5,6] and compounds (TiW and Ta–Si–N) [7,8] have been proposed. Among the proposed diffusion barriers, Ta has been widely investigated as a single metal diffusion barrier for Cu metallization because it not only has a melting point (2996 °C) and silicidation temperature ( ≈ 650 °C), but it also shows a very low solubility in Cu [9,10].

For instance, the barrier properties of a sputtered Ta barrier layer, where Ta layer thickness is 50 nm, were stable up to 500 °C [6]. In the case of a Ta 50 nm thickness barrier deposited by electron beam evaporation, it also prevented interaction between Cu and Si up to 550 °C [11].

Ta, which is one of the refractory metal barriers, is known to have no reaction or compound with respect to Cu because of a thermodynamically stable interface in the Cu/Ta contact system [9]. This indicates that Cu diffusion through the barrier layer—in particular its grain boundaries and other microstructure defects—forms Cu silicides at the barrier/Si interface, resulting in failure of the diffusion barrier. This reveals that in order to enhance the barrier properties for Cu/barrier/Si contact systems, the interface of the Cu/barrier and

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barrier/Si substrate should be controlled. The thermal stability Cu/barrier and barrier/Si interface is another important parameter that controls the properties of a diffusion barrier.

Previous studies have revealed PVD deposited Ta films to be excellent metallurgical diffusion barriers between copper and Si [12,13]. However, their processes have serious limitations owing to the poor step coverage caused by the shadowing effect for small feature sizes ( $<0.35$ µm) and high aspect ratio contact and via holes. Accordingly, Ta barriers deposited by chemical vapor deposition (CVD) have received much attention owing to their superior conformality compared to sputtered-Ta barriers. However, it is well known that CVD-Ta has poor metallurgical stability and much higher resistivity than physical vapor deposited (PVD)-Ta.

In our present work, Ta barriers were prepared by ionized metal plasma (IMP) sputtering as a deposition technique. It will overcome the generic PVD processing limitations, such as the poor step coverage, without losing the excellent metallurgical diffusion barrier properties. IMP deposition results in denser Ta film microstructures, particularly at grain boundaries. Hence, the diffusion and intermixing of Cu through Ta film can be blocked effectively due to the discontinuous grain boundaries and it is expected that the barrier properties be much improved over those from CVD-Ta films. The test sample structure is Cu(200 nm)/Ta(30 nm)/$SiO_2$(250 nm)/Si and the diffusion barrier properties were evaluated by electrical measurements. Furthermore, XRD, SEM, SIMS, TEM and RBS were employed in conjunction with electrical measurements to examine the failure mechanism.

## 2. Experimental procedure

All sample preparation and experiments described in this study used 8″ Si (100) wafers. Si wafers were cleaned in 10:1 diluted HF solution and rinsed in deionized water before $SiO_2$ deposition. First, a 500 nm thick plasma enhanced chemical vapor deposited (PECVD) $SiO_2$ dielectric was deposited by using a gas mixture of $SiH_4$, $O_2$ and Ar at 400 °C on 8″ Si wafers. The $SiO_2$ deposited Si substrates were loaded into the IMP sputtering chamber for the deposition of Ta (30 nm) and subsequently Cu (200 nm) without breaking the vacuum. The IMP deposition process has been described in detail elsewhere [14]. The samples were annealed in $N_2$ ambient up to 950 °C from 350 °C with 100 °C intervals. The resistivities of as-deposited and annealed samples were measured by four-point probe (Tencor Flexus 2320) to survey the overall reactions involving Cu. The surface morphology and grain size were examined by atomic force microscopy. AFM was performed using a Nanoscope III multimode atomic force microscopy. Data were collected in tapping mode AFM with silicon cantilevers at resonance frequencies in the range of 200–300 kHz. The X-ray diffraction (XRD) measurements were performed with a RIGAKU model RINT2000 diffractometer using a $\gamma = 2.5°$ grazing incident angle geometry. The $CuK_\alpha$ X-ray ($\lambda = 1.542$ Å) detection was carried out from $2\theta = 20–85°$ with scan speed of 4° per minute and scan step 0.05° for the analysis of reaction product phases and the interdiffusion of the elements across the interface, respectively. The surface morphologies of the structure at various temperatures were observed by JEOL 5410 scanning electron microscope (SEM) employing a 20 keV primary electron beam. The hetero-interfaces of the structure at various temperatures were characterized by JEOL 200LX transmission electron microscope (TEM). RBS spectra were taken with 2 MeV $He^+$ ions at a scattering angle of 160° using a 50 $mm^2$ passivated implanted planar silicon (PIPS) detector of 14 keV resolution. SIMS analysis was carried out in a Cameca IMS6f magnetic sector instrument. An $O_2^+$ primary ion beam was used with a beam current of 90 nA and a primary ion energy of 12.5 keV.

## 3. Results and discussion

Fig. 1 shows the XRD pattern obtained from as-deposited Ta diffusion barrier layer. Pure Ta sputtered in pure Ar ambient on $SiO_2$ grows as the high-resistivity (200 µΩ-cm) tetragonal metastable phase and apparently polycrystalline. The XRD pattern reveals that the peaks centered approximately at 33.55°, 38.2° and 64.65° were correspond to those of tetragonal β-Ta and were indexed to the (111), (211) and (122), respectively. The Cu film sputtered deposited on Ta diffusion barrier has a strong (220) preferred orientation at $2\theta$ angle of 74.1°, but low intensity peaks of (111) and (200) were also observed.

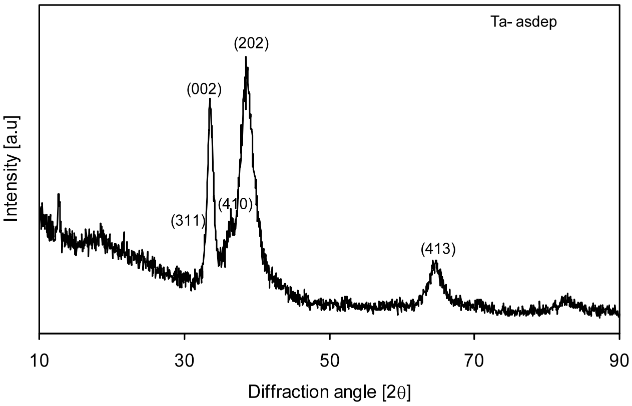

Fig. 1. XRD pattern obtained from as-deposited Ta diffusion barrier on PECVD–$SiO_2$.

The surface morphology and grain size were examined by atomic force microscopy. AFM measurement demonstrates a smooth and nonporous surface morphology with a surface roughness (rms) of ≈0.2912 nm for a 30 nm Ta film, documented by the AFM surface plot of Fig. 2(a), which consisted of small grains with a mean grain size of ≈5 nm. Cu film had a grain size of ≈80 nm (Fig. 2b) with a roughness of ≈1.309 nm. The crystalline Cu sample exhibits small bumps, which correspond to the columnar structure of the film.

Fig. 3(a) shows a TEM image of the as-deposited Cu/Ta/$SiO_2$/Si structure, which reveals a flat, discrete interface between Cu and β-Ta. The Cu film deposited on Ta diffusion barrier shows a typical columnar structure. As shown in Fig. 3(a), the Ta film looks dark compared to the Cu layer, since Ta is a much heavier element. The cross-section TEM micrograph of the Cu/Ta/$SiO_2$/Si structure before annealing shows that the metal layers are uniform, discrete and planar, implying that the as-deposited sample is free from contamination or oxidation caused by the environment. Fig. 3(b) shows a magnified Cu layer whose grain boundaries are perpendicular to the surface and interface. This TEM image also supports the columnar structure of the Cu film. The arrows in the figure point where the grain boundaries are situated.

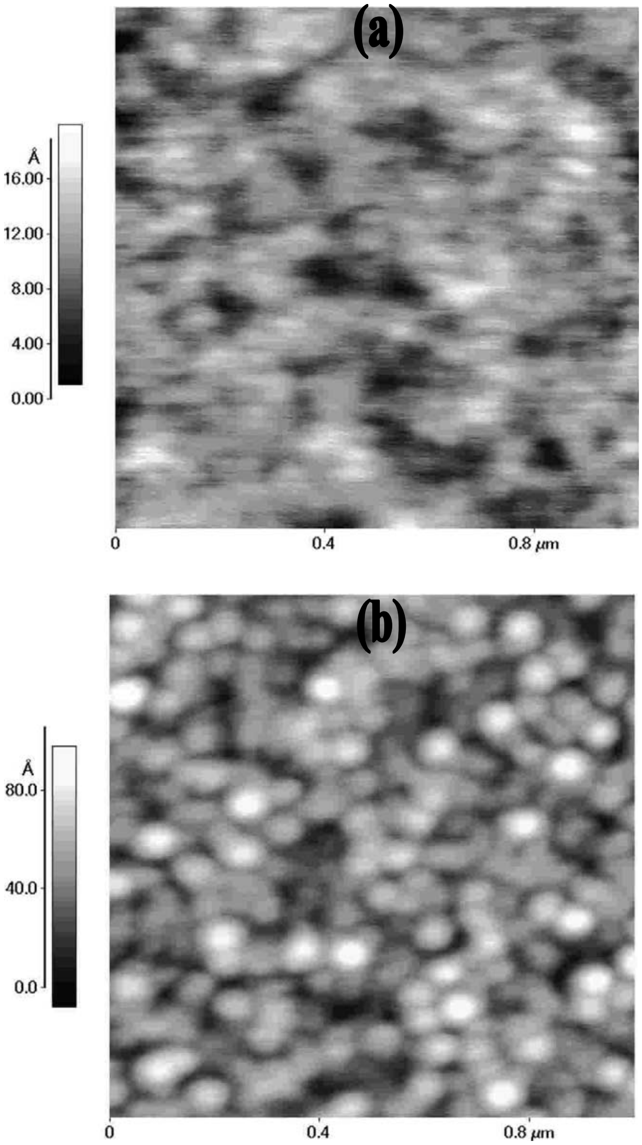

Fig. 2. AFM measurement results for IMP-deposited (a) Ta diffusion barrier with roughness (rms) ≈0.2912 nm and grain size ≈10 nm and (b) Cu metallization layer with roughness (rms) of ≈1.3094 nm and grain size ≈90 nm.

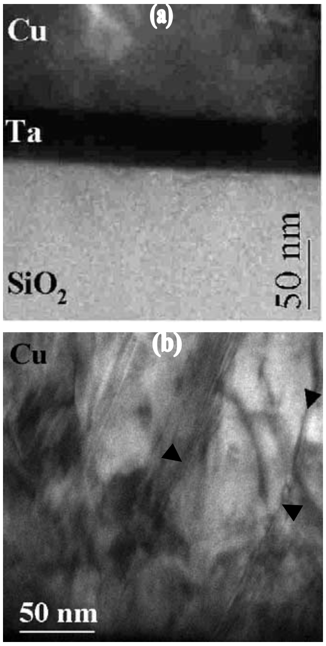

Fig. 3. TEM image of the as-deposited sample showing smooth Cu/Ta and Ta/$SiO_2$ interfaces (a). TEM image (b) shows Cu layer with grain boundaries perpendicular to the surface and interface which indicates the columnar structure of Cu film.

The graph presented in Fig. 4 indicates the change in sheet resistance measured on the Cu/Ta/$SiO_2$/Si structure as a function of annealing temperature in $N_2$ ambient for 35 min. Two major opposing trends characterize the change in sheet resistance after anneal-

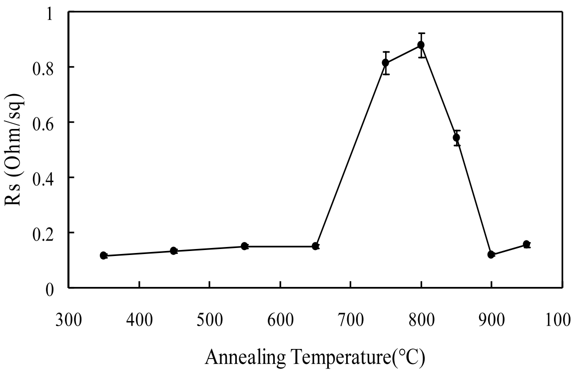

Fig. 4. Sheet resistance of Cu/Ta/$SiO_2$/Si structure as a function of annealing temperature.

ing 650 °C, an abrupt rise in sheet resistance of the multilayer sample on annealing at 650 °C and drops back to a low value after 800 °C annealing. It must be realized that the top Cu layer of 200 nm carries nearly all the current, the sheet resistance measurements monitor the condition and the quality of the Cu overlayer. Hence, this curve can be used to estimate the degree of intermixing, reaction and changes of integrity across the metallization layers as well. According to this figure, all samples annealed up to 650 °C can maintain the same level of sheet resistance as the as-deposited sample. Two major opposing trends characterize the change in sheet resistance after annealing 650 °C. In the sheet resistance measurements of $Cu/Ta/SiO_2/Si$ multilayer, the measured layer is Cu, into which contaminants can penetrate either from its underlayer or from the ambient. As the latter is not evident in backscattering spectra (see RBS results), it seems reasonable to assume that an interaction and/or intermixing of the Cu layer with the underlying Ta is the main cause of the observed changes in electrical measurement. Hence, the extent to which the resistance increases should be expected to correlate with the quantity of Ta that penetrates the Cu layer. The abrupt rise in sheet resistance after 650 °C for $Cu/Ta/SiO_2/Si$ structure is primarily attributed a partial intermixing between Cu and the underlying films and/or a symptom of a catastrophic failure caused by an overall reaction involving all the metallization layers. The sheet resistance of the $Cu/Ta/SiO_2/Si$ structure drop back to a very low value after 800 °C annealing is probably due to (i) the β-Ta (tetragonal) to α-Ta (body centered cubic) phase transformation, since β-Ta has a resistivity of 200 μΩ-cm and α-Ta phase has a relatively low value, 30 μΩ-cm; (ii) the structure behaves as an intrinsic semiconductor since the underlying silicon is now carrying almost all the probe current. The first assumption is based on the facts that β-Ta might out-diffuse to Cu film and contribute to a rise in sheet resistance measurement. When the temperature reached 800 °C, transformation from β-Ta to α-Ta phase might have brought the sheet resistance back to a low value. It is also reported that the phase transformation of Ta starts at ≈800 °C for a Ta film alone without Cu and a slightly lower temperature for Cu/β-Ta structure [15]. Another element that can give low resistivity value in the test structure is Si, which also might interdiffuse with Cu through Ta. This behavior is similar to that observed in an investigation carried out by Holloway et al. [6].

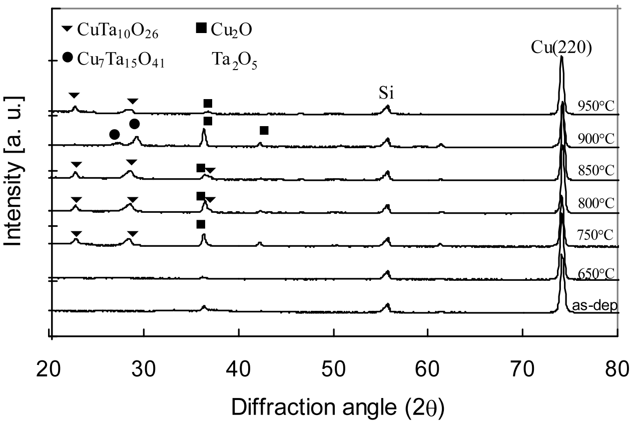

Fig. 5. XRD patterns of the $Cu/Ta/SiO_2/Si$ structure annealed at various temperatures in $N_2$ ambient for 35 min.

The grazing incident angle of 2.5° identified the intermixing and new phase formation for the $Cu/Ta/SiO_2/Si$ structure annealed up to 950 °C. As shown in Fig. 5, there is a distinction in XRD spectra between samples annealed below and above 750 °C. Below 750 °C, only a strong pure Cu (220) peak was found at 74.1°. Any reaction involving Cu, Ta, O or Si was not observed. A major change in XRD spectra occurred after annealing at 750 °C. As expected, the main observed peaks for the 750 °C annealed sample are $Ta_2O_5$ (001), (200) at $2\theta°$ angles of 22.90, 28.50° and $Cu_2O$ (111), (220) and (220) at 36.90°, 42.36° and 61.45°, respectively. $Cu_2O$ (111) appeared very close to the peak of Ta. A strong pure Cu (220) peak is still preserved through annealing process. The small peaks of $CuTa_{10}O_{26}$ (200) and (1 19 1) at 28.7° and 37° were also clearly observed after annealing at 800 °C. The peak intensities of $Ta_2O_5$ and $Cu_2O$ were more pronounced after annealing at 800 °C and a new weak peak $CuTa_{10}O_{26}$ (1 19 1) appeared $2\theta = 36.9°$ in the pattern, while a sharp and strong peak of $Cu_2O$(111) remained. With annealing at 950 °C, the new compound $Cu_5Ta_{11}O_{30}$ (0 0 10) and (112) turns up at $2\theta°$ angles of 27.40° and 29.25°. It is thought that the formation of these compounds primarily attributed to the rapid increase in sheet resistance, as shown in Fig. 4. On the other hand, according to XRD and RS measurement results, the formation of $Cu_2O$, $Ta_2O_5$ and $Cu_5Ta_{11}O_{30}$ compounds seem to govern the changes in sheet resistance. They would, however, contribute to the rise in sheet resistance value after 650 °C annealing, but not the drop back after 800 °C based on the published information. Hence, the only possible reason for the sheet resistance drop back to a very low value is the phase transformation of Ta and Ta-based compounds, such as $Ta_2O_5$ and $Cu_5Ta_{11}O_{30}$, in this case. But to the best of our knowledge, there is no information on the phase transformation of such compounds (Ta-based compounds) and related resistivity drop. However, no $Cu_xSi_y$ and $Ta_xSi_y$ formation were observed in the XRD spectrum, indicating that no reactions occurred between Cu and Si, Ta and Si in the structure or the amount might be under detection limits of XDR analysis. Hence, it is reasonable to exclude the out-diffusion of Si to Cu layer and the second assumption for resistivity drop in Fig. 4. Formation of Cu, Ta and Cu–Ta oxide might hinder the diffusion of Cu, so that

Cu silicide formation will not be available up to elevated temperature.

But there is no clear indication of α-Ta to β-Ta phase transformation in the XRD result or the diffraction peak of α-Ta phase did not appear in the XRD spectra of the Cu/Ta/$SiO_2$/Si multilayer structure until after annealing 850 °C was presumably (i) due to the small amount α-Ta that was below detection limits of the XRD analysis; (ii) not all the β-Ta changed to α-Ta at the same time and temperature; or (iii) the out-diffusion of Ta is randomly distributed rather than uniform throughout the Cu layer and most of the Ta atoms easily oxidized to $Ta_2O_5$.

Rutherford backscattering spectrometry (RBS) was used to examine reaction and interdiffusion between the Cu metallization layer and Ta diffusion barrier. Fig. 6 shows the RBS depth profile of the Cu/Ta/$SiO_2$/Si sample annealed for 35 min at various temperatures. The surface scattering energies for O, Si, Cu and Ta are indicated. The discrete layer of Ta and Cu peaks are clearly seen in the sample without annealing. The Ta layer appears to remain largely intact up to 350 °C and no evidence of intermixing was observed, as shown in Fig. 6. However, the width of the Cu peak increases while the height decreases, indicating that the Cu oxidation process has started. When annealing temperature reached 550 °C, there was a shift in the Ta peak towards the surface (Fig. 6). This can be attributed to the thickness variations in the Cu layer as the tailing edge of the Cu peak also shift about the same amount, but the integrity of the structure remains. The occurrence of the small surface peak, after annealing at 650 °C corresponding to that of Ta, indicates that a small amount of Ta has diffused to the surface of the sample. For the sample annealed at 750 °C, the motion of Ta atoms toward the Cu surface gradually proceeds and the tailing edge of Cu becomes smoother. The motion of Ta elements are clearly observed in the RBS spectra, since a new Ta peak appears at the higher energy levels. At the same time, the gradient of the trailing edge of the Cu signal changes for the sample annealed at 850 °C. This fact implies that Ta atoms have reached and accumulated at the Cu surface and indicate a possible formation of a mixed (Cu–Ta) layer. The following features were also observed for all samples annealing temperature higher than 650 °C: (i) a significant reduction of the Ta peak height and the broadening of the Ta peak width; and (ii) the tailing of Cu peak into even lower energy. These appearances further indicate the formation of Cu–oxide and the agglomeration process of Cu film. When the temperature reaches 950 °C, a new Ta peak that appeared at the energy level of 1.836 MeV became more prominent, indicating that Ta atoms had seriously migrated to the surface, giving a peak in the RBS signal at the surface energy expected for Ta. The back edge of the Cu signal also becomes more graded and smooth with increasing temperature, implying that Cu film has agglomerated, thus exposing part of the Ta film to the ambient which is consistent with the SEM observation results. The gradient also implies the penetration of Cu to $SiO_2$/Si substrate layer.

The cross-sectional TEM view from the sample annealed at 800 °C is presented in Fig. 7(a). At the center of the figure, there is a large nodule, which extends into the Cu layer to a significant depth, determined by the position lying immediately to the side of the nodule. The composition of the nodule was confirmed to be (Cu, Ta, O) with energy dispersive spectroscopy (EDS) attached to TEM. The illustration shows that the annealing at 800 °C results in a reaction in several places. The interface become somewhat corrugated and moreover, some Ta grains seem to move into the Cu film. The reaction product (Cu–Ta oxide) is in contact with the underneath $SiO_2$, as well as along the Cu grain boundaries that are perpendicular to the surface and interface. Most of the metallic Ta layer remains between Cu and $SiO_2$. It is also noticed that the interface between Ta and $SiO_2$ is still very sharp and Cu–Ta oxide has no reaction with $SiO_2$. On the other hand, some dark grains are found to form within the Cu layer. Energy dispersive spectroscopy (EDS) analysis results reveal that those grains are Ta which have out-diffused. It was reported that it is possible for Ta to diffuse outwards due to its high affinity towards oxygen, if there is enough available in the ambient. On the other hand, the columnar structure of Cu film enhances the migration of Ta to Cu film. Diffusion of Ta into the Cu seem to start along the grain boundaries in the range ≈ 550–600 °C. The faster lattice diffusion of Cu compared with Ta, it is not necessary for Cu to move first at this interface. On the other hand, oxygen as the residual gas from furnace ambient can diffuse through Cu grain boundaries to Ta and form $Ta_xO_y$ due to the strong oxygen affinity of Ta at the interface of Cu/Ta where the Cu grain boundaries terminated.

TEM results from the sample annealed at 900 °C, which are presented in Fig. 7(b), display a crystalline layer with thickness locally as high as 100 nm at the interface of Cu and Ta. Although electron diffraction data from the precipitate cannot be obtained, the effective barrier thickness decreases seriously owing to the interaction between Cu, Ta and oxygen, which means that Ta thin film is a sacrificial barrier between $SiO_2$ and Cu. However, the Ta layer is not completely consumed by the reactions and remains in some regions. Since the formation of precipitates were found inside Cu layer, it is clear that Ta atoms diffused to Cu film and on the way to the Cu surface it reacted with oxygen, Cu and/or $Cu_2O$ and initially formed $CuTa_{10}O_{26}$ compound and then $Cu_5Ta_{11}O_{30}$.

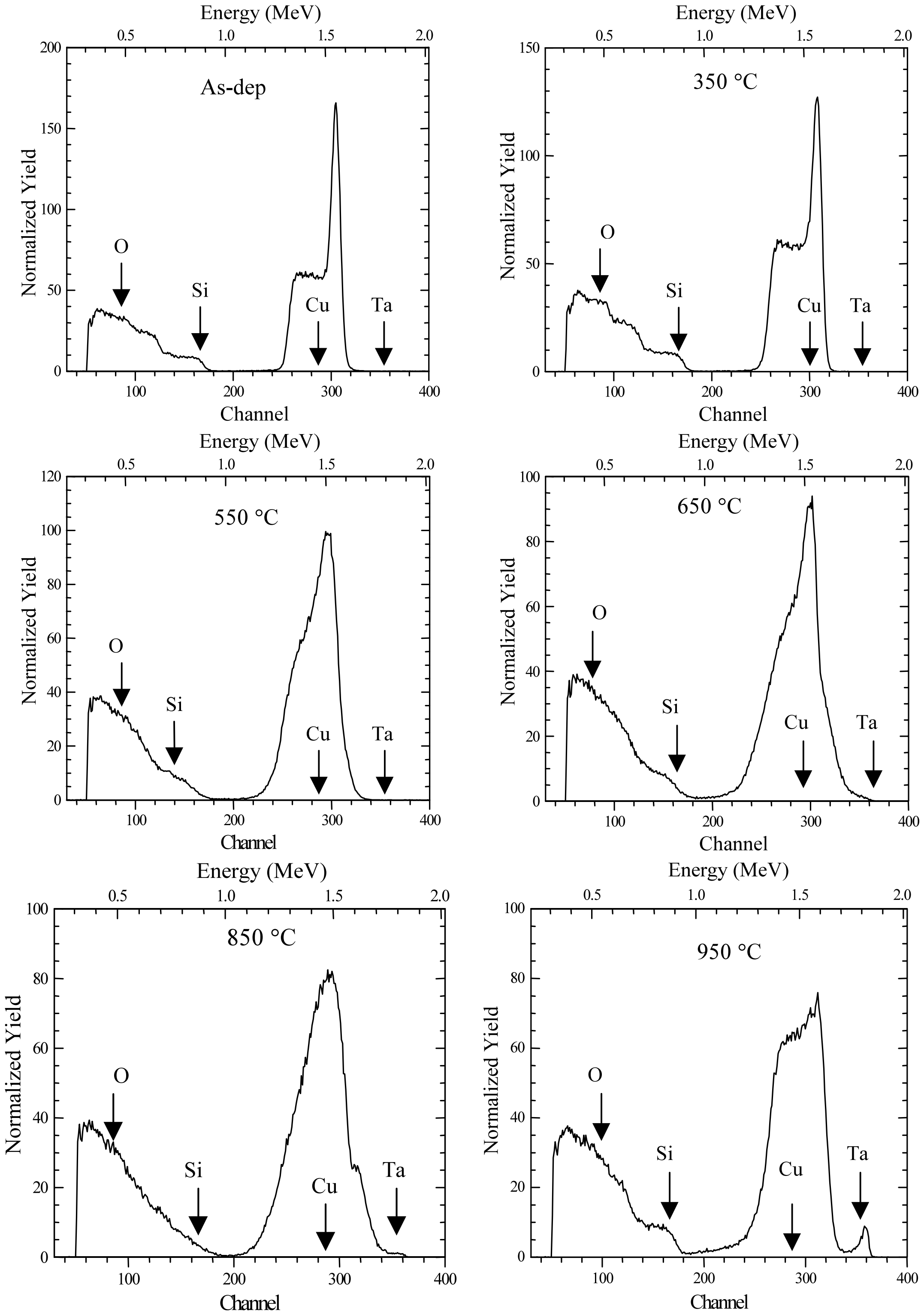

Fig. 6. RBS spectra for Cu/Ta/SiO$_2$/Si structure as deposited and annealed at various temperatures in N$_2$ ambient for 35 min.

The mechanisms of the Cu film oxidation at low temperatures were studied by Li et al. [16]. It was observed that Cu is first oxidized to Cu$_2$O at the temperature as low as 200 °C then CuO at 300 °C. The oxidation starts at the Cu surface and progress slowly into the bulk. Since inward diffusion of oxygen proceeds gradually as a function of annealing time, the complete oxidation from Cu$_2$O to CuO depends on the annealing condition. In the present experiment, the samples were protected by the inert N$_2$ ambient during

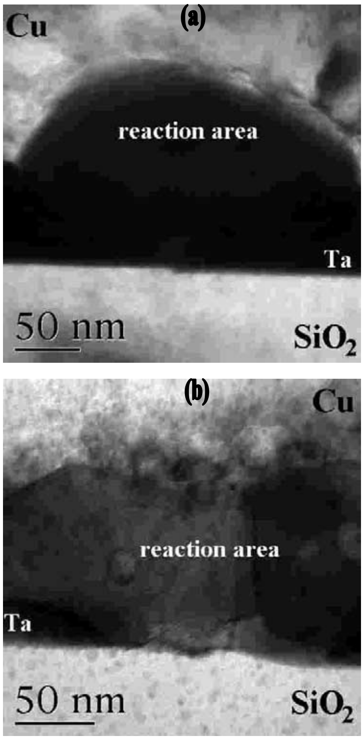

Fig. 7. TEM images of the Cu/Ta/SiO$_2$/Si multilayer structure after annealing at (a) 800 °C and (b) 900 °C in N$_2$ ambient for 35 min.

annealing process the formation temperature of Cu$_2$O increased significantly and no formation of CuO was observed in the XRD result. In the case of Ta$_2$O$_5$, according to the Ta–O binary system, up to $\approx 30$ at.% of the oxygen could be interstitially dissolved in the b.c.c-Ta lattice prior to conversion into the amorphous or polycrystalline Ta$_2$O$_5$ phase [17]. The solubility of oxygen in the metastable β-Ta is not known accurately, but it has to be larger than that of stable α-Ta. The larger solubility of oxygen into the β-Ta layer is expected to rule out the possibility that segregation of oxygen in the grain boundaries of Ta film. As impurity in polycrystalline Ta films, O is believed to increase the effectiveness of the diffusion barrier by decorating the extended defects, such as grain boundaries, thereby blocking the active paths for grain boundary diffusion [7]. On the other hand, it was reported that Ta has very high affinity to oxygen and forms one stable oxide, Ta$_2$O$_5$ [18]. Once the oxide layer has formed, it may retard diffusion of Cu through Ta layer. The dissolution of oxygen into the Ta rich layer will take place when the intrinsic diffusion coefficient of oxygen in the Ta layer is high enough. Since the intrinsic diffusion coefficients are exponentially dependent on temperature, the kinetic of the dissolution reaction change strongly with temperature [19].

It is clear that even at an annealing temperature lower than 650 °C, the Cu and Ta start to react with the O$_2$ existing in their respective grain boundaries, producing Cu$_2$O and Ta$_2$O$_5$. By annealing at 800 °C, a new peak of CuTa$_{10}$O$_{26}$ appeared, probably due to the reaction among Ta$_2$O$_5$, Cu$_2$O, Ta and Cu at the interface of Cu/Ta. Hence, it is though that during annealing process, oxygen atoms might play an important role in the phase transformation and Cu, Ta and Cu–Ta oxides formation in the structure. It is necessary to find out the sources of oxygen which contribute to the phase transformation as well as the formation of Cu$_2$O, Ta$_2$O$_5$ and CuTa$_{10}$O$_{26}$ during the annealing process.

The first source is oxygen atoms incorporated in the Ta metal film from the deposition ambient during the Ta deposition and decorating the grain boundaries [11]. Fig. 8(a) shows the oxygen and carbon concentration and the depth profile in IMP-Ta, being examined by SIMS analysis. The presence of oxygen in the Ta layer is indicated indirectly by the formation of metastable β-Ta, which is in the body centered cubic (b.c.c) lattice structure with only slight tetragonal distortion. Another source of oxygen atoms is from the SiO$_2$, which would diffuse into and/or react with the Ta layer, as the annealing temperature increased since Lane et al. reported the possible reactions between SiO$_2$ and Ta and the formation of Ta$_2$O$_5$ [20]. Lastly, oxygen atoms can be incorporated from the annealing ambient, since the Cu metallization layer was observed to have a columnar structure diffusion of oxygen through the channel between the grains into the Cu/Ta interface might occur in a reasonable time scale. The oxygen profile, as measured by SIMS in different annealing temperature, proved the diffusion of oxygen from both ambient and SiO$_2$, as presented in Fig. 8(c).

Even though there is no clear indication of the β-Ta (tetragonal) to α-Ta (body centered cubic) phase transformation in the XRD result, it is suggested that the mechanism of the polymorphic transformation is the dissolved oxygen in the octahedral sites of the b.c.c lattice [21]. This would lead to the tetragonal structure with a $c/a$ ratio $<1$, as has been previously observed. The incorporation of oxygen of more than 2–3 at.% in the Ta layer at the annealing temperatures used in this study leads to the formation of stable oxide Ta$_2$O$_5$ and eventually to the formation of b.c.c Ta [22]. The oxygen dissolved during the heat treatment, in addition to the oxygen already incorporated into the Ta film during the deposition, can lead to a situation where the Ta matrix is unable to dissolve all the oxygen at low temperatures and therefore a stable oxide layer is formed at the interface of Cu/Ta.

Fig. 8 shows the SIMS depth profiles of the structure after annealing at 650, 750 and 850 °C. As shown in Fig. 8(b), there is a significant increase in the Ta level in the Cu layer, while the Cu distribution exhibits a tail extended into the Ta layer. This SIMS result indicates significant interaction at the metal–barrier interface. There may be some Cu–Ta–O layer formation at the

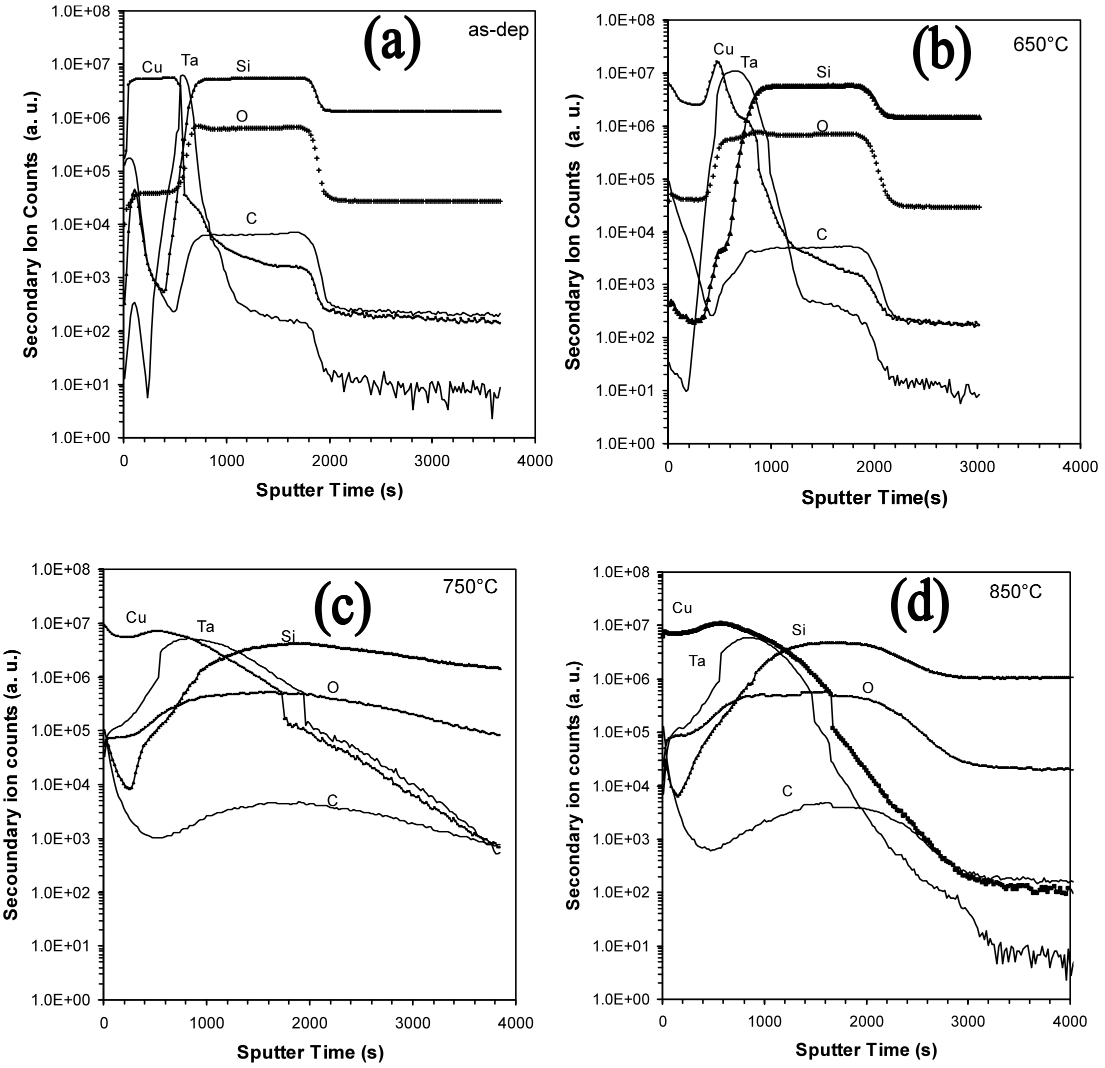

Fig. 8. SIMS depth profiles of the Cu/Ta/$SiO_2$/Si multilayer structure (a) before and after annealing at (b) 650 °C, (c) 750 °C and (d) 850 °C in $N_2$ ambient for 35 min.

interface. On the other hand, a small amount of Ta has already accumulated at the Cu film surface. Increasing the annealing temperature to 750 °C (Fig. 8c), SIMS depth profile of the sample in which an extensive interdiffusion of Cu and Ta was found. But some Cu diffused through the Cu–Ta oxide layer and piled up at the interface of Ta and $SiO_2$, since the Cu signal still exist under the Ta signal. It reveals the fact that more reactions among Cu and Ta atoms takes place in the presence of oxygen in their grain boundaries and from the $SiO_2$ layer. Hence, oxygen SIMS signal moving towards Cu film through Ta barrier will cause more Ta out-diffusion into Cu and more Cu–Ta oxide layer formation. There is a significant increase in the Ta level in the Cu layer, as shown in Fig. 9(d), while the Cu distribution exhibits a tail extended into the $SiO_2$/Si substrate in the sample annealed at 850 °C. The SIMS results indicate significant interaction at the metal–barrier interface. There may be some Cu–Ta oxide and/or Ta oxide formation at the interface of Cu/Ta, but a considerable amount of Cu diffused into $SiO_2$/Si. Cu diffusion seems to occur after the grains of reaction products no longer maintained its continuity due to stress. Part of Cu layer already reacted with oxygen, Ta and/or $Ta_2O_5$ and formed $Cu_2O$ and $Cu_xTa_yO_z$ at lower temperature ($\approx$750 °C), initially in order that heavy diffusion of Cu cannot be expected. This was supported by the XRD result in which no significant change in Cu (220) was observed throughout the annealing process. Although SIMS data revealed that Ta was diffused into $SiO_2$, there is no $Ta_xSi_y$ formation observed in XRD result because (i) since Ta is very affinity to oxygen so that Ta–O was form first; (ii) $Ta_xSi_y$ formation temperature is higher than that of Ta oxides, [23]; and (iii) Ta oxide has no reaction with $SiO_2$.

The equilibrium diagram indicates that there are no intermetallic compounds in the Cu/Ta binary system. Thus, at the Cu/Ta interface, the diffusion of one or

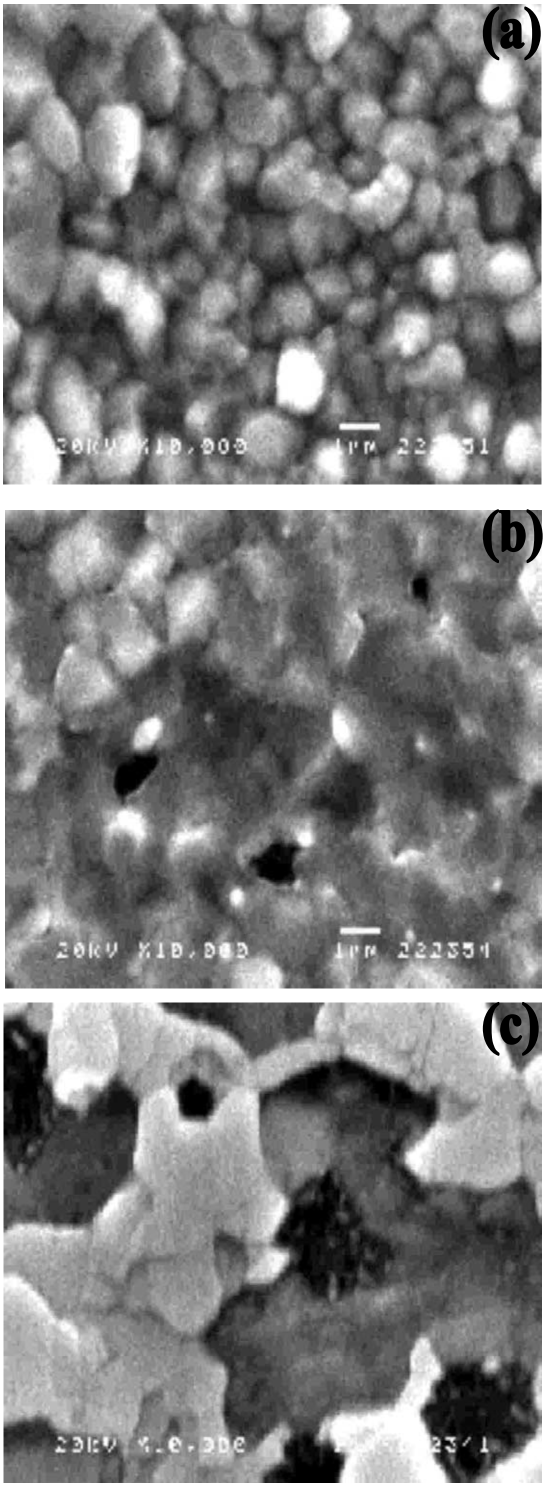

Fig. 9. SEM images of Cu/Ta/$SiO_2$/Si multilayer structure after annealing at (a) 650 °C, (b) 750 °C and (c) 850 °C in $N_2$ ambient for 35 min.

both of the elements is the only expected phenomenon. At a first approximation, Cu is expected to be the moving species at the interface due to its much lower melting point in comparison that of Ta. However, it is still possible for Ta to diffuse outwords, due to its high affinity towards oxygen, if there is enough available in the Cu film as well as in the annealing ambient. The out-diffusion of Ta and the amorphous layer formation were previously reported [15]. It seems that Ta was the main moving species during the reaction and Cu just offered short-circuit diffusion paths for the Ta phase transformation. During the phase transformation, the β-Ta thin film was broken at some locations and the α-Ta grains grew inside the Cu layer.

Fig. 9 shows the surface morphologies of Cu/Ta/$SiO_2$/Si film annealed at various temperatures in $N_2$ ambient for 35 min. The average grain size of an as deposited Cu was ≈30 nm and it grew as annealing temperature increased. SEM micrographs show that the copper surface did not exhibit any change up to 650 °C (Fig. 9a) and patches were observed at 750 °C (Fig. 9b) and grew with the increasing temperature. Average grain size after annealing at 650 °C was ≈1 μm as shown in Fig. 9(a). Annealing temperatures higher than 650 °C, Cu film starts to agglomerate due to the accelerated grain growth in Cu film. At 750 °C, Cu grains agglomerated each other disclosing part of Ta to the ambient. These patches might be the part of Ta film exposed to the ambient due to Cu film agglomeration. Energy dispersive spectroscopy (EDS) analysis was performed on the patches and the agglomerated Cu film for the sample annealed at and beyond 800 °C. It revealed that the patches had much lower Cu concentration than the other area, supporting that the patches might be the part of Ta film exposed to the ambient due to Cu film agglomeration.

The behavior of agglomeration varied significantly with the nature of the annealing ambient. But it is well known that agglomeration of Cu film results from grain growth induced by the oxidation of the film. The reason for grain growth is not fully understood, but residual stress is considered the most probable candidate affecting grain growth of the films [24]. In general, the stress can be divided into two types, intrinsic and extrinsic. The first type originated from various factors, such as lattice mismatch between the thin film and the substrate, impurities, defects and chemical reaction etc. The oxidation of Cu films fixed at Ta/$SiO_2$/Si substrate is considered to produce significant compressive residual stress due to volume expansion resulting from Cu oxide formed in Cu film. It has been reported that oxygen incorporated Ta also induced an increase in compress stress in the film [25]. It was clear that the oxygen was incorporated in the Cu and Ta films during deposition and annealing process. Oxygen may exist as Cu oxide at surface or grain boundaries of Cu film because the solubility of the oxygen in Cu is extremely low at temperatures below 450 °C [26]. Due to the thin oxide (copper oxides) formed on Cu surfaces, the surface energy of Cu grains or the stress of the film will change and these variations may cause the accelerated grain growth. However, normal grain growth was observed for this sample in $N_2$ ambient at 650 °C, as shown in Fig. 9(a). The grain size of 200 nm thick Cu film became five times larger than its thickness, which is sufficient to induce agglomeration. As a consequence, large Cu grains will induce a thermal groove [27] reaching a substrate (Ta/$SiO_2$) resulting in agglomeration of the film.

However, in all the above results, an increase in sheet resistance by four points probe, the formation of $Cu_2O$ and $Ta_2O_5$ by XRD and the accelerated grain growth observed by SEM agree well and simultaneously occurs at around 650 °C. According to RBS and SEM results, Ta has reached and accumulated on the Cu surface, since Ta had migrated to the Cu surface, giving a peak in RBS signal at the surface energy expected for Ta. The out-diffusion of the Ta that accumulates on the surface has been reported earlier [6]. During annealing, Ta atoms preferentially penetrate through the grain boundaries or thermally-induced microcracks of the Cu film and on the way to the Cu surface it reacted with the oxygen residing in the grain boundaries of Cu film, Cu atoms and/or $Cu_2O$ and formed $Ta_xO_y$ and $Cu_xTa_yO_z$. By comparison to Ta, Cu that has larger grain size, in other words the widely open grain structure, will serve the fast diffusion paths for Ta (grain size 10–20 nm) to migrate to the Cu surface.

## 4. Conclusion

The diffusion barrier properties of IMP deposited Ta film between Cu and $SiO_2$ have been investigated in the Cu (200 nm)/Ta (30 nm)/$SiO_2$(250 nm)/Si multi-layer structure. The 30 nm thick IMP-Ta was found to be stable up to 650 °C. During post deposition annealing, several phenomena occurred: (i) the Ta atoms migrated to Cu film and appeared on the Cu surface; (ii) $Cu_2O$ and $Ta_2O_5$, formed due to $O_2$, mainly exist in the grain boundaries; (iii) due to the reactions between $Cu_2O$, Ta, Cu and $Ta_2O_5$, a new compound $Cu_xTa_xO_z$ was produced; and (iv) the accelerated grain growth of Cu film and agglomeration uncovered the underneath film, Ta. However, no evidence of Cu diffusion through the Ta diffusion barrier ($Cu_xSi_y$ formation) was observed up to 950 °C annealing.

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