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Behaviour of ionized metal plasma deposited Ta diffusion barrier between Cu and SiO_2

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This work investigated the diffusion barrier properties of ionized metal plasma (IMP) deposited Ta between Cu and SiO_2. When Cu and Ta layers were formed by IMP sputtering, it was found that the Cu has the equilibrium f.c.c. structure with the grain size of 80 nm whereas Ta is in a metalstable tetragonal (β-Ta) form with a grain size of around 10 nm. With the help of sheet resistance measurement, X-ray diffraction, cross-section transmission electron microscope analysis, Rutherford backscattering spectroscopy, secondary ion mass spectroscopy, and scanning electron microscopy, the Ta barrier layer was observed to fail at temperature above 650°C due to the reactions among Cu, Ta and O and formation of $Cu_xTa_yO_z$. The phase transformation of β-Ta into the stable phase (α-Ta), in the presence of Cu was encountered when annealing the sample at above 800°C. The role of oxygen was also found to be important in the phase transformation, in the reactions and it seems to have a strong effect on the thermal stability of the barrier layer.

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1. Introduction

Copper is expected to come into widespread use as an interconnecting metal line in microelectronic devices and packaging applications. The demand for increasing of 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 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

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order to enhance the barrier properties for Cu/barrier/Si contact systems, the interface of the Cu/barrier and barrier/Si substrate should be controlled. The thermal stability Cu/barrier and barrier/Si interface are another important parameters that control 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 (less than 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 procedures

For 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 microscope. 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 K_α Cu X-ray ($\lambda = 1.542$ Å) detection was done from $2\theta = 20°$ to $2\theta = 85°$ with scan speed of 4°/min 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 annealing temperature 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 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 Cu/Ta/SiO_2/Si structure. Pure Ta sputtered in pure Ar ambient on SiO_2 grows as the high-resistivity (200 $\mu\Omega$-cm) tetragonal metastable phase and apparently poly crystalline. The XRD pattern (inset) 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 (002), (202) and (413) respectively. The Cu film sputterd deposited on Ta diffusion barrier has a strong (220) preferred orientation at 2θ angle of 74.4° but low intensity peaks of (111) and (200) were also observed.

The surface morphology and grain size were examined by atomic force microscopy. AFM measurements 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. 2a, which consists of very fine grains with a mean grain size of ∼10 nm. The crystalline Cu sample exhibits small bumps with grain size of about ∼80 nm and a roughness of around ∼1.309 nm as shown in Fig. 2b. These bumps may correspond to the columnar structure of the film.

Fig. 3 shows the TEM images of the as deposited Cu/Ta/SiO_2/Si structure, which reveal the flat, discrete

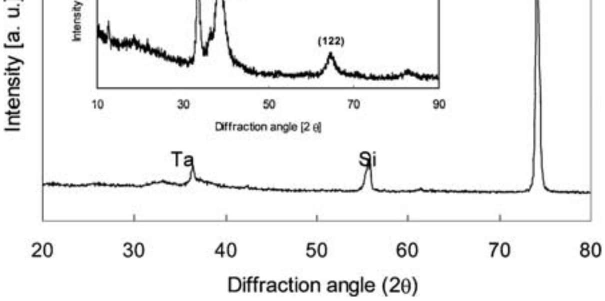


Figure 1 XRD spectrum of the as-deposit Ta film deposited on SiO_2 layer grown as β-Ta phase.

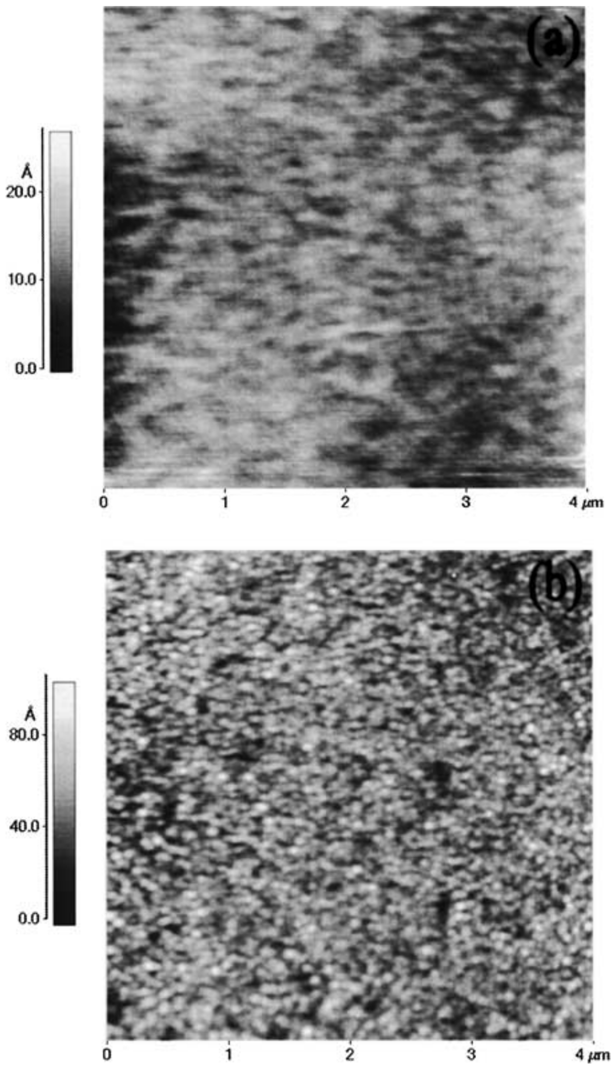


Figure 2 AFM measurement results for IMP-deposited (a) Ta diffusion barrier with roughness (rms) ~0.2912 nm and grain size ~10 nm and (b) Cu metallization with roughness (rms) of ~1.3094 nm grain size ~90 nm.

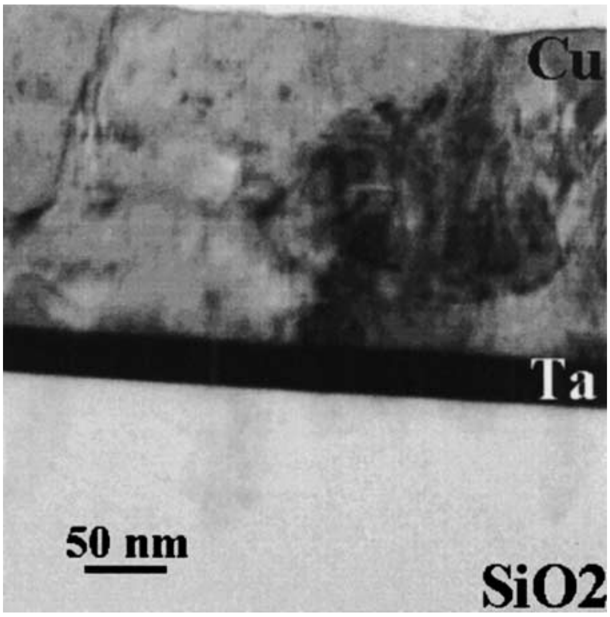


Figure 3 Cross-sectional TEM picture of an as-deposited sample Cu/Ta/SiO_2/Si multilayer structure showing no diffusion or intermixing at the two interfaces.

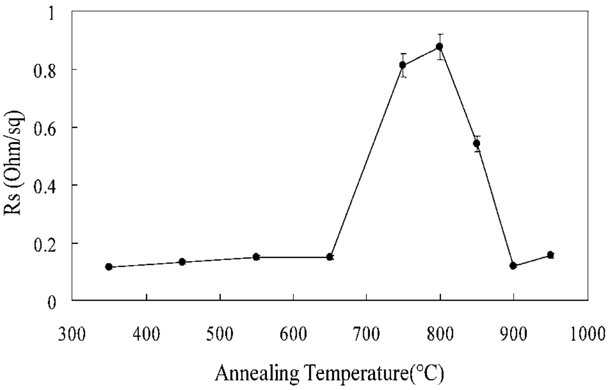


Figure 4 Sheet resistance of Cu/Ta/SiO_2/Si structure as a function of annealing temperature.

interfaces between Cu and β-Ta. The Cu film deposited on Ta diffusion barrier shows a typical columnar structure. 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. There is no evidence of reaction or intermixing at any interface.

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 temperatures in N_2 ambient for 35 min. The measured sheet resistance values were dominated by the copper thin film since the copper film (200 nm and 1.72 $\mu\Omega$-m) is much thicker and has a markedly lower resistivity than Ta film (30 nm and 200 $\mu\Omega$-cm) and any reaction products. Since 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, these curves 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 samples. Two major opposing trends characterize the change in sheet resistance after annealing 650°C. 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 since the resistance of thin film is sensitive to contamination. In our case, 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 result), it seems reasonable to assume that an interaction of the Cu layer with the underlying Ta is the main cause of the observed changes. Hence, the extent to which the resistance increases should be expected to correlate with the quantity of Ta that penetrates the Cu layer. The sheet resistance of the Cu/Ta/SiO_2/Si structure drops 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 $\mu\Omega$-cm and α-Ta phase has a relatively low value, 15 $\mu\Omega$-cm [15]; (ii) the structure behaves as an intrinsic semiconductor since the underlying silicon

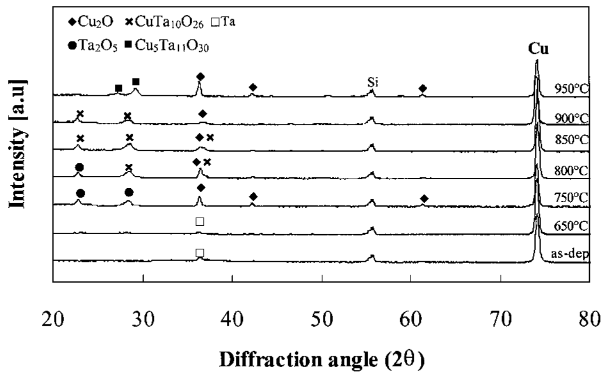


Figure 5 XRD patterns of the Cu/Ta/SiO_2/Si structure annealed with various temperatures.

is now carrying almost all of the probe current and this behavior is similar to that of observed in previous investigation [6] and (iii) both might be occurred at the same time. It is also reported that the phase transformation of Ta starts at about 800°C for a Ta film alone without Cu and a slightly lower temperature for Cu/β-Ta structure [16].

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. Annealing temperatures lower than 750°C, only a strong pure Cu (200) peak is found at 74°. Any reaction involving Cu, Ta, O or Si was not observed. Distinctly, at 750°C, several new peaks were found which were identified as Ta_2O_5 (001), (200) at 2θ° angles of 22.90, 28.50° and Cu_2O (111), (220) and (220) at 36.90°, 42.36° and 61.45° respectivey. Cu_2O (111) appeared very close to the peak of Ta. The peaks with low intensities of $CuTa_{10}O_{26}$ (200) and (1 19 1) at 28.7° and 37° were also clearly observed after annealing at 800°C. These peaks became more prominent and were observed very close to tantalum pentoxide (Ta_2O_5) peaks as the annealing temperature reached to 850°C. With annealing at 900°C, the new compounds $Cu_5Ta_{11}O_{30}$ (112) and (118) turns up to 2θ° angles of 27.40° and 29.25°. This observation leads to the conclusion that the formation of these compounds primarily attributed the changes in sheet resistance as shown in Fig. 4. On the other hand, there is no Cu_xSi_y compound formation was found and no significant reduction in Cu (220) peak was observed in the XRD result, it can be ruled out that neither Cu diffusion through the Ta barrier nor out diffusion of Si to the Cu film was taking place. On the other hand, the escalation of resistance measurement at and above 650°C was not due to the lost of conductive Cu layer and the probes are detecting the high resistivity Ta layer. Therefore, formation of Cu_2O, Ta_2O_5 and $Cu_5Ta_{11}O_{30}$ compounds seem to govern the changes in sheet resistance. They would contribute 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 compound 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 and related resistivity drop.

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. This would lead to the tetragonal structure with the c/a ratio smaller than 1, as has been previously observed [17, 18]. 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_2O_5 and eventually the formation of b.c.c Ta (α-Ta) [19]. 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 not able to dissolve all the oxygen at low temperatures and therefore a stable oxide (Ta_2O_5) layer is formed at the interface of Cu/Ta [19]. On the other hand, it was also reported that an amorphous layer (contain Cu and Ta) formation was fund to be take place between Cu and β-Ta thin film by interdiffusion between Ta and Cu. The presence of the amorphous layer seems to play an important role in the transformation of β-Ta to α-Ta transformation that took place between 500 and 800°C [16]. But, 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 both of the elements is the only expected phenomenon. At a first approximation, Cu is expected to the moving species at the interface due to its much lower melting point in comparison that of tantalum. However, it is still possible for Ta to diffuse outwards, due to its high affinity towards oxygen, if there is enough available in the Cu film. The stresses incorporated in to the Ta film during the deposition also enhance the diffusion of Ta. The out diffusion of Ta and accumulated at the surface of Cu film was previously reported [9]. It seems that Ta was the main moving species during this reaction (between Cu and Ta and formation new phase) and Cu just offered short circuit diffusion paths for the Ta phase transformation. By compare to Ta, Cu that has larger grain size, in other words, the widely open grain structure will serve the fast diffusion paths for Ta to migrate to the Cu surface. During the phase transformation, the film was broken in some locations and the α-Ta grew inside the Cu layer. According to this observation the Cu and α-Ta will give a low resistivity value than that of Cu and β-Ta. In our XRD result, the formation of $CuTa_{10}O_{26}$ was observed first annealing temperature at 750°C and the sheet resistance drop back after 800°C annealing, due to the β-Ta to α-Ta phase transformation, was somehow similar to the result reported by Lee *et al.* [16]

On the other hand, Clevenger *et al.* [15] reported that the high temperature polymorphic tantalum phase transition from the tetragonal β-Ta phase to the cubic α-Ta phase causes a large decrease in the resistance of thin film and a complete stress relaxation in films that were intrinsically compressive stressed. It is thought that the formation of Cu_2O, Ta_2O_5 and $CuTa_{10}O_{26}$ will

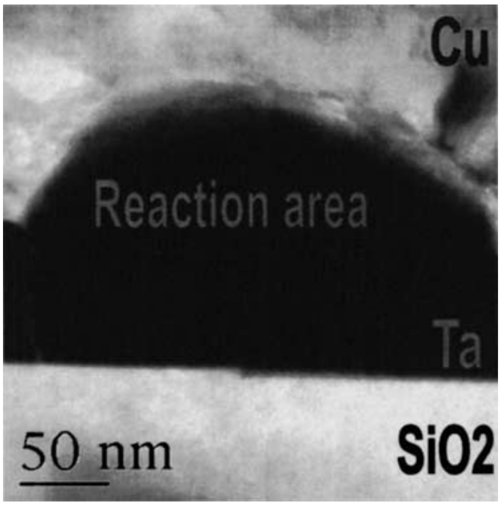


Figure 6 TEM micrograph of the Cu/Ta/SiO_2/Si multilayer structure after annealing at 800°C.

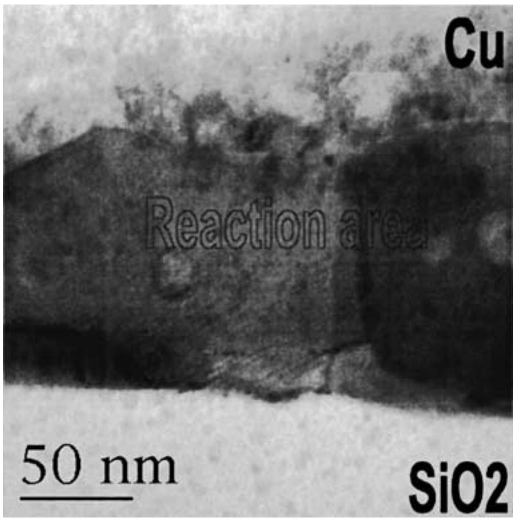


Figure 7 TEM micrograph of the Cu/Ta/SiO_2/Si multilayer structure after annealing at 900°C.

increase the compressive stress in the respective film and at the interface. This compressive stress from those compound seem to become the driving force for the phase transition from the tetragonal β-Ta phase to the cubic α-Ta phase.

The cross sectional TEM view from the sample annealed at 800°C is presented in Fig. 6 in which Ta film look dark and the Cu film are light since the Cu film are lighter since Ta is a much heavier elements. At the center of the figure there is a large precipitate, which extends into the Cu layer to a significant depth, determined by the position lying immediately to the side of the precipitate. The composition of the precipitate was confirmed to contain Cu, Ta and O with EDS (energy dispersive spectroscopy) attached to TEM. As the Ta atoms migrated to the Cu region, the thickness of Ta seems to be wider in Cu region compare to as-deposited value shown in Fig. 3. This observation supports the out diffusion of Ta atoms to the Cu metallization layer. However, it is very difficult to know whether the phase is α-Ta or β-Ta at this stage since the grains are too small for through electron diffraction analysis. On the other hand, part of β-Ta atoms were already reacted with oxygen and transformed to Ta_2O_5 so that it is hard to receive peaks for α-Ta and/or β-Ta in XRD result. The reaction products were formed sporadically only on the Cu side of Cu/Ta interface after 800°C and XRD result identified the precipitate as $CuTa_{10}O_{26}$.

Further evidence of this can be seen in Fig. 7 where TEM result from the sample annealed at 900°C is presented. Fig. 7 displays 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 can not be obtained, the effective barrier thickness decrease seriously owing to the interaction between Cu and Ta layer, which means that Ta thin film is a sacrificial barrier between SiO_2 and Cu. The Ta layer is not completely consumed by the reaction and still 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 Cu surface it was reacted by oxygen, Cu and/or Cu_2O and formed $CuTa_{10}O_{26}$ first and then $Cu_5Ta_{11}O_{30}$.

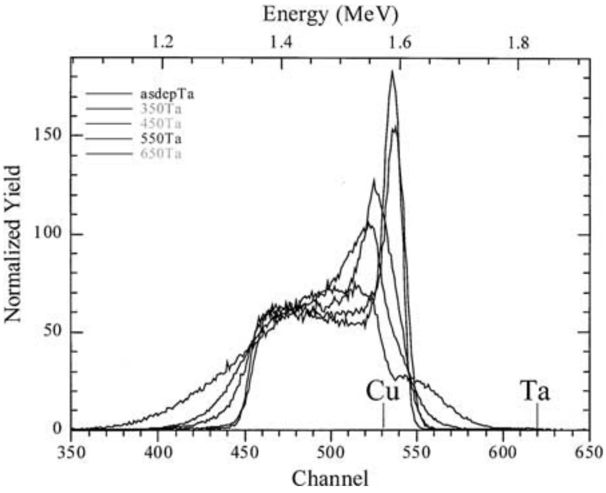


Figure 8 RBS spectra for Cu/Ta/SiO_2/Si structure as deposited and annealed for 35 min at 350, 450, 550 and 650°C.

Rutherford backscattering spectrometry (RBS) was used to examine reaction and interdiffusion between the Cu metallization layer and Ta diffusion barrier. Figs 8 and 9 show 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 as-deposited film exhibits two separable Ta and Cu peaks without evidence of intermixing. The Ta layer appears to remain largely intact up to 450°C. For the sample annealed at 550°C, the motion of Ta atoms toward the Cu surface gradually begun, but the integrity of the structure is still remained. For the sample annealed at 650°C (Fig. 8), the motion of elements are more clearly observed and the RBS spectra show that the gradient of the trailing edge of the Cu signal changes and a small amount of Ta appears at the higher energy levels. The following features were observed for samples annealing temperature higher than 650°C (i) a significant reduction of the Ta peak height and the broadening of the Ta peak (ii) the tailing of Cu peak into even lower energy. These features indicate a possible formation of a new (Cu-Ta) compound. When the temperature reaches 800°C (Fig. 9), a new Ta peak appears at the energy level of 1.836 MeV and grows indicating

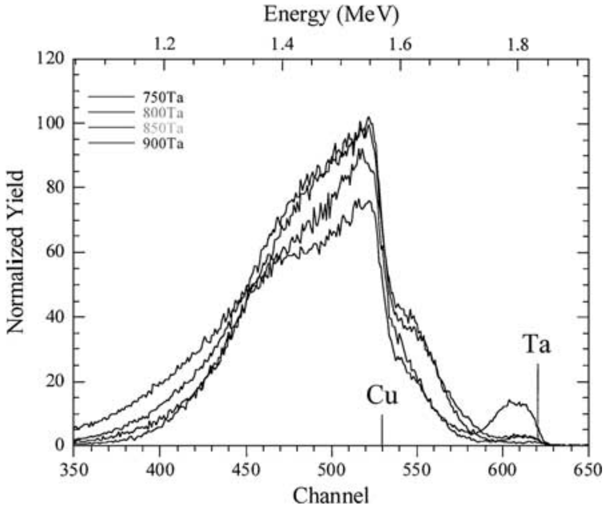


Figure 9 RBS spectra for Cu/Ta/SiO_2/Si structure annealed for 35 min at 750, 800, 850, and 900°C.

that Ta had 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 becomes more graded with increasing temperature, implying that Cu film starts to agglomerate, thus exposing part of the Ta film to the ambient.

The mechanisms of the Cu films oxidation at low temperatures were studied by Li *et al.* [20] It was observed that Cu is first oxidized to Cu_2O at the temperature as low as 200°C. Since the samples were protected by the inert N_2 ambient during annealing process the formation temperature of Cu_2O increased significantly and no formation of CuO was observed. For the case of Ta_2O_5, according to the Ta-O binary system, up to approximately 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_2O_5 phase [21]. The solubility of oxygen in the metalstable 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]. The dissolution of oxygen in to 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. So that only at 750°C annealing temperature the dissolution oxygen, which existing in their (Cu as well as Ta) respective grain boundaries, to Cu and Ta or formations of Cu_2O and Ta_2O_5 were observed in XRD spectra. By annealing at 800°C, a new peak of $CuTa_{10}O_{26}$ appeared, probably due to the reaction among Ta_2O_5, Cu_2O, Ta and Cu at the interface of Cu/Ta. Hence, this observation reveals the fact that the oxygen in this structure play an important role in the reactions and it seem to have the strong effect on the thermal stability of the barrier layer.

It is necessary to know the sources of oxygen, which contribute the formation of Cu_2O, Ta_2O_5 and $CuTa_{10}O_{26}$. Firstly, oxygen atoms 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_2O_5 [22]. The SIMS result for the sample annealed at 750°C (Fig. 10c) reveals the movement of oxygen peak from SiO_2 toward Ta layer. The second source is oxygen atoms incorporated in the Cu and Ta metal films from the deposition ambient during the Cu and Ta deposition and decorating the grain boundaries [11]. Fig. 10a shows the oxygen and carbon concentration and the depth profile in Cu/Ta/SiO_2/Si, 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. Lastly, oxygen atoms can be incorporated from the annealing ambient, since the Cu metalization layer was observed to have a columnar structure diffusion of oxygen through these channels between the grains into the Cu/Ta interface might occur in a reasonable time scale. There is a different in O peaks profile in as-deposit and annealed at 850°C provide another evidence of oxygen diffusion form the annealing ambient.

Fig. 10 shows the SIMS depth profiles of the structure after annealing at 650, 750 and 850°C. As shown in Fig. 10b, 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 results indicate significant interaction at the metal–barrier interface. There may be some Cu-Ta-O layer formation, but a very small amount of Ta out diffusion into Cu film surface. Increasing the annealing temperature to 750°C, (Fig. 10c), SIMS depth profile of the sample in which an extensive inter-diffusion of Cu and Ta was found. But, some Cu diffused through the Cu-Ta oxide layer and pile up at the interface of Ta and SiO_2 since the Cu signal still exit under the Ta signal. It reveals the fact that more reactions among Cu and Ta atoms taking placed at the present of oxygen in their grains boundaries and from the SiO_2 layer since oxygen SIMS signal moving towards Cu film through Ta barrier will cause more Ta out diffusion in 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. 10d, 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 seem 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 (~750°C) first so that heavily diffusion of Cu cannot be expected. This was supported by the XRD result in which no significant changes in Cu (200) was observed throughout the annealing process.

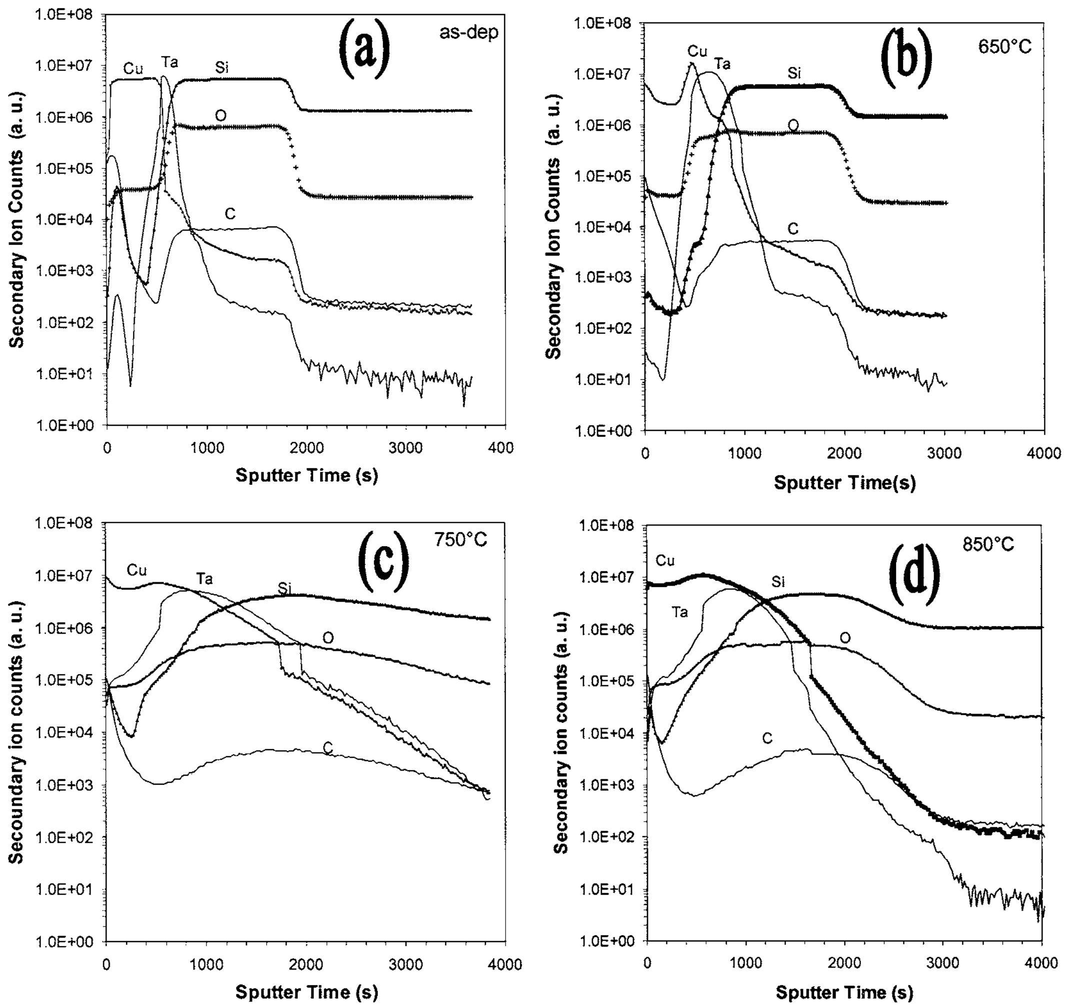
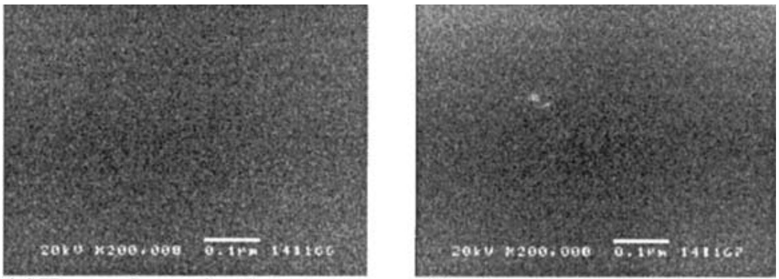


Figure 10 SIMS depth profiles of the Cu/Ta/SiO_2/Si multilayer structure (a) before and after annealing at (b) 650°C, (3) 750°C, and (4) 850°C in N_2 ambient for 35 min.

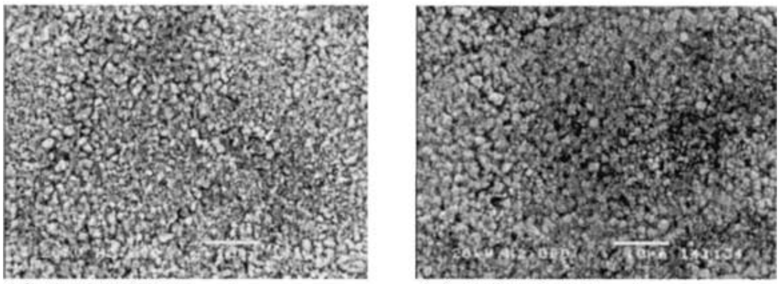
Although SIMS data revealed that Ta was diffused into SiO_2 there is no Ta_xSi_y formation was observed in XRD result because (i) since Ta is very affinity to oxygen so that Ta-O was form first, (ii) Ta_xSi_y formation temperature is higher than that of Ta oxides, [23] and (iii) Ta oxide has no reaction with SiO_2.

Fig. 11 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 about 80 nm and it grew as annealing temperature increased. SEM micrographs show that the copper surface did not exhibit any change up to 650°C except grain growth and patches were observed at 750°C and beyond and grew with the increasing temperature. Average grain size after annealing at 650°C was about 4–5 times larger than as-deposited grain size as shown in Fig. 11b and e. Annealing temperatures higher than 750°C, Cu film starts to agglomerate due to the accelerated grain growth in Cu film. At 850°C, Cu grains agglomerated each other disclosing part of Ta to the ambient as clearly can see by Fig. 11f. These patches might be the part of Ta film exposed to the ambient due to Cu film agglomeration. EDS (energy dispersive spectroscopy) 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.

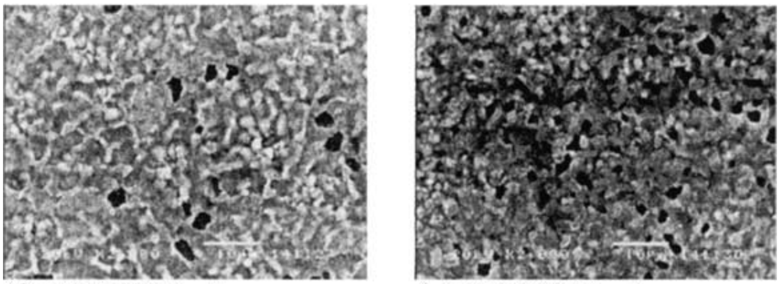
Besides grains boundary energy reduction, surface energy and strain energy reductions are the driving forces for grains growth in thin films [24, 25]. Due to the thin oxide (copper oxides) formed on Cu surfaces, the surface energy of Cu grains or the stress of the film will change, and these variations may cause the accelerated grain growth. It was reported that normal grain growth occurs until the nominal grain size of the film becomes 2–4 times larger than the film thickness, while abnormal grain growth gives a preferential growth of some grains [26, 27]. Zielinski *et al.* [25] reported that if surface energy and stress variation were significantly different with different orientations of grains, some specially oriented grains would grow abnormally to reduce the total system energy. Conversely, if surface energy and stress variation are uniform with the orientation of the grains, abnormal grain growth will not be observed. In our present work, no evidence of abnormal grain growth in Cu film was observed during thermal annealing. As shown in Fig. 5, a Cu (220) preferred orientation was maintained through out the annealing process, and no abnormal grains were observed in SEM images. These facts reveal that normal grain growth occurs in this Cu film during the annealing process. On the other hand, it is not likely that the uniform variation



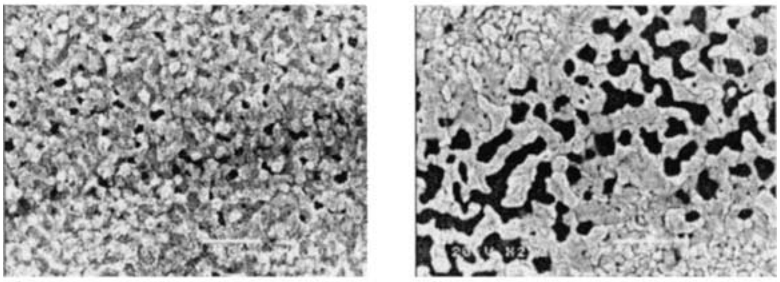
(a)**Ta-as deposited** (b) **Cu on Ta as-deposit**



(d) **550 °C/ 35 min** (e) **650 °C/ 35 min**



(f) **750°C/ 35 min** (g) **850°C/ 35 min**



(h) **900°C/ 35 min** (i) **950°C/ 35 min**

Figure 11 SEM micrograph of the Cu/Ta/SiO_2/Si multilayer structure annealed at various temperature.

of surface energy with grain orientation induces the grain growth in thin films [28]. Since the volume of grain boundaries reduces during the grain growth, tensile stress is produced in film. As a consequence, only a compressive stress condition can be relaxed by grain gowth [28, 29]. Halliday *et al.* also reported that the oxidation of Cu increased the compressive stress in the film due to the formation of a superficial oxide layer [30]. This suggests the fact that compressive stress induced from the oxidation of Cu becomes the driving forces for the normal grain growth of Cu thin film.

In contrast, the ratio of the film thickness (h) to the grain size (D) is the important factor in determining the possibility of agglomeration [31]. If h/D ratio is large, the free surface will become a circular cap before the thermal groove reaches the underlayer so that the continuity of the film is maintained. However, if h/D ratio is small, the thermal groove will be able to reach the under layer, which will result in the agglomeration of the film [32]. Therefore, in the two films with the same thickness and different grain sizes, the film with larger grains agglomerates to become a discontinuous morphology during thermal annealing. However, 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 after 650°C annealing.

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 (500 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 were occurred: (i) the Ta atoms migrated to Cu film and appeared on the Cu surface, (ii) Cu_2O and Ta_2O_5 were form 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, (iv) the sheet resistance of the structure has shown opposite trend after annealing at 650°C and (v) 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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