Effect of oxygen on the reactions in the Si/Ta/Cu metallization system

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The effect of oxygen on the reaction mechanisms in the Si/Ta/Cu metallization system was studied experimentally and by utilizing the thermodynamically assessed Ta–O binary system. It was presented that an interfacial tantalum oxide was formed between Cu and Ta and that it established an additional barrier layer for Cu diffusion. The formation of additional barrier layer was supported by the following observations: (i) No detectable amount of Cu was found from the Ta layer with the combined transmission electron microscopy and energy dispersive spectroscopy at temperatures as high as 650 °C. (ii) Secondary ion mass spectrometry measurements indicated that significant amount of oxygen was incorporated into the films already after the sputtering stage. (iii) $^{181}Ta^{16}O$ molecular ion signals were detected from the Ta/Cu interface, indicating that the additional layer was in fact some form of tantalum oxide. The diffusion of Cu through the Ta layer could not proceed until the interfacial oxide had been dissolved by the Ta matrix. Since the oxygen solubility in Ta matrix is high in the temperature range of interest, the interfacial oxide dissolution was kinetically controlled. It is to be noted that the threshold temperature range of the dissolution reaction was found to coincide with that of the β–Ta to the bcc-Ta transition, which was anticipated to enhance the kinetics of the dissolution.

I. INTRODUCTION

Cu interconnections have been attracting more attention since the introduction of the first functional microprocessors fabricated with this technology.[1] Although Cu offers many advantages in comparison to Al-based materials, it requires a capping layer to prevent diffusion of Cu into Si and into dielectric materials used. Tantalum and its compounds are among the most widely investigated diffusion barriers for Cu metallization.[2–10] The effect of oxygen on the stability of Ta diffusion barrier layers has been previously shown to be substantial.[9] However, the reason for that is not yet clear. It has been argued, for example, that oxygen is present at the grain boundaries and is blocking there the fast grain boundary diffusion of Cu. This is not probably the correct explanation, since the solubility of oxygen in Ta is large in the temperature range of interest, which does not favor strong segregation of oxygen into grain boundaries of Ta.[11] On the other hand, on the basis of the thermodynamics as well as of the results from the literature (e.g., Ref. 12), the formation of an amorphous TaO_x layer at the Ta/Cu interface is more likely.[10] The prediction is supported by the experimental observation that no extensive diffusion of Cu into Ta layer was detected with the energy dispersive spectroscopy (EDS) up to 650 °C. Furthermore, the abrupt nature of the reaction, after only a relatively small temperature increase (35 °C up from 650 to 685°C), suggested the disappearance of the additional barrier layer from the interface. Therefore, it is expected that only after a certain threshold temperature range has been reached, the relaxation of the kinetic constraints enables the dissolution of the interfacial oxide into the Ta matrix, after which diffusion of Cu can proceed. The predicted interfacial oxide formation is further supported by the observations made by Chen *et al.*,[13] which showed that even sub-monolayer coverages of oxygen on polycrystalline tantalum affect strongly the kinetics of Cu diffusion in Ta. Moreover, in two very recent papers,[14,15] direct evidence of the existence of the TaO_x layer at the Ta/Cu interface was presented with the help of detailed TEM analyses. In this paper, the effect of oxygen on the reactions in the Si/Ta/Cu metallization system is investigated experimentally and by employing the phase stability information. The thermodynamic basis for the interfacial oxide formation, as observed recently,[14,15] will be presented. Finally, the effect of the Ta film thickness is discussed.

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II. MATERIALS AND METHODS

The copper and tantalum films were sputter-deposited onto cleaned and oxide-stripped (100)-oriented *n*-type Si substrates in a dc/rf-magnetron sputtering system in argon atmosphere. The thicknesses of the tantalum layers were about 10, 50, and 100 nm. Using x-ray diffraction (XRD), the Ta layers were determined to have the metastable tetragonal β–Ta structure. Copper films with a thickness of 100 nm on the 10–50-nm Ta films and 400 nm on the 100-nm Ta barrier films were subsequently deposited in the same sputtering system without breaking the vacuum. The base pressure before the deposition runs was about 3×10^{-5} Pa. The samples were annealed in the vacuum of 10^{-4} Pa at temperatures ranging from 400 to 800 °C for 30 min. The reaction products in the Si/Ta/Cu metallization scheme were characterized by XRD, Rutherford backscattering spectrometry (RBS), and transmission electron microscopy (TEM) combined with EDS. Secondary ion mass spectrometry (SIMS) was used to measure the depth distribution of oxygen in the metallization structure. XRD analyses were conducted with Seifert XRD 3000 TT (Ahrensburg, Germany) vertical theta–theta diffractometer using a Cu tube, 40-kV voltage, and 25-mA current. RBS measurements were performed with a 2 MeV He^+ ion beam normal to the surface, with a scattering angle of 170°. TEM investigations were conducted with JEOL 2000FX (Tokyo, Japan) operated at 200 kV. SIMS measurements were done with 12 keV Cs^+ ions for the Si/Ta(10 nm)/Cu(100 nm) and Si/Ta(50 nm)/Cu(100 nm) samples. The detected area was about 10% from the scanned area to avoid the crater sidewall contributions to the depth profile. The layers in the Si/Ta(100 nm)/Cu(400 nm) samples were found to be in practice too thick to be used in the SIMS analyses. The results obtained from the thinner films are nevertheless expected to be applicable also to the thick films as discussed below. The calculation of the oxygen solubility in Ta was based on the assessed experimental binary thermodyanmic data.

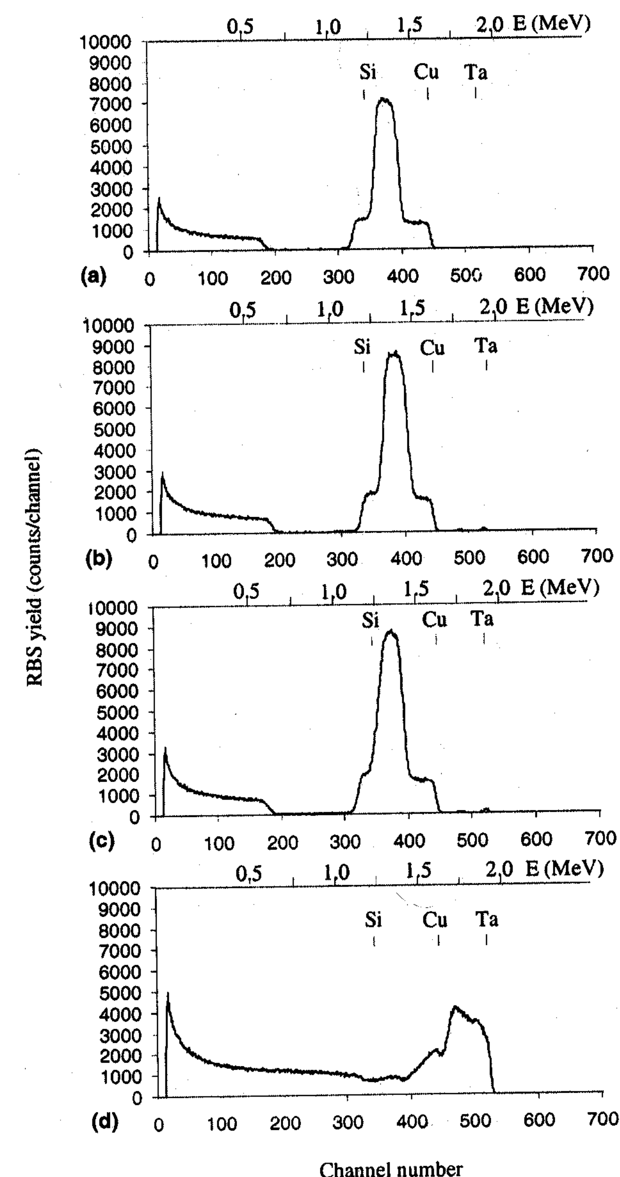

FIG. 1. RBS spectra (2.0 MeV 4 He^+, θ = 170°) from the Si/Ta(100 nm)/Cu(400 nm) samples with (a) no annealing and annealed at (b) 625 °C, (c) 675 °C, and (d) 685 °C. Vertical marks represent surface scattering energies.

III. RESULTS AND DISCUSSION

The reactions in the samples, with the 100-nm-thick Ta diffusion barrier layer, are anticipated to proceed in the following manner during the annealings. According to the RBS and XRD results shown in Figs. 1 and 3, respectively, the reactions in the metallization structures set in at 685 °C. RBS reveals some interdiffusion between Ta and Cu at 625 °C, as indicated by a small Ta surface peak corresponding to small amount of tantalum diffusing to the sample surface. Ta diffusion toward the surface has been observed previously.[3,4] Diffusion of Ta may occur if there is a trace amount of water vapor in the vacuum system, since Ta has a very high affinity to oxygen: first by dissolving it and then by forming metastable or stable oxides being in local equilibrium with the saturated solid solution. However, as the oxidizing of Ta is known to be controlled by inward diffusion of oxygen into the metal,[16] the occurrence of the Ta surface peak is not expected to be explained this way. It is also possible that stresses incorporated into the Ta film during the deposition stage enhance the diffusion of Ta. Previous investigations have shown that a strong gradient of force gives rise to a mean diffusion velocity for the affected atoms.[17] At this stage the exact nature of the Ta "outdiffusion" is not clear and requires further investigations. The strongly columnar structure of the Cu overlayer (Fig. 2) enables oxygen diffusion from the ambient

through the Cu layer to the Ta/Cu interface. This oxygen will have a significant role in the reactions taking place at the higher temperatures. XRD analyses show the formation of $TaSi_2$ and Cu_3Si at 685 °C (Fig. 3), but according to the cross-sectional TEM analyses, the formation of $TaSi_2$ has already started at 650 °C (Fig. 2). The formation of Cu_3Si can not be detected with XTEM at 650 °C, suggesting that the diffusion of Cu through the

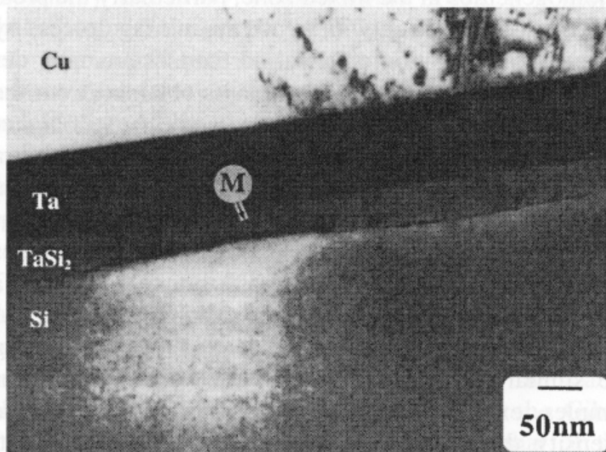

FIG. 2. Bright field TEM image from the Si/Ta(100 nm)/Cu(400 nm) sample annealed at 650 °C showing the columnar grain structure of $TaSi_2$ designated as M.

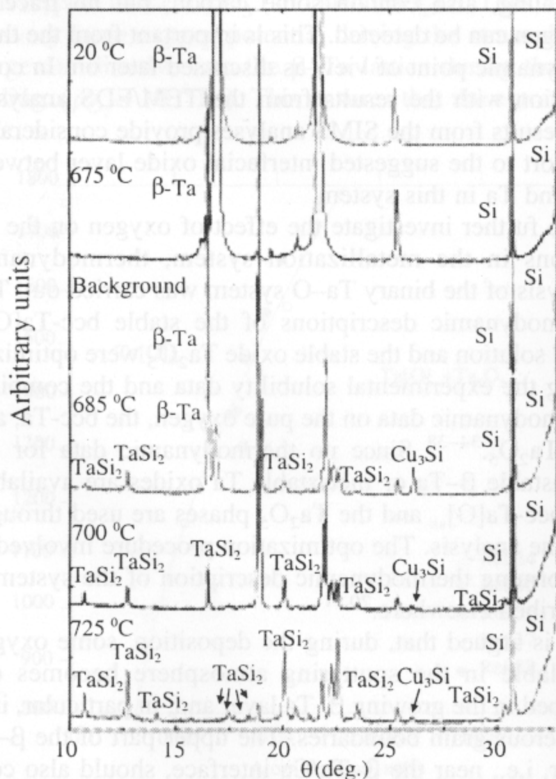

FIG. 3. XRD spectra from the Si/Ta(100 nm)/Cu(400 nm) samples annealed at different temperatures.

Ta layer is not yet significant. This is confirmed with the EDS analyses (results not shown), which do not show any significant traces of Cu inside the Ta layer. This is not expected, since both the Ta and $TaSi_2$ layers have columnar microstructures, thus providing many high-diffusivity paths for Cu migration. Most likely, the penetration of Cu into Ta is slowed down by an interfacial oxide layer. In fact, the presence of the TaO_x interfacial layer between Ta and Cu in similar metallization system has been observed recently with the detailed cross-sectional TEM analysis.[14,15] The additional barrier layer postpones the diffusion of Cu up to a temperature range where the dissolution of the layer from the interface becomes kinetically possible. Only after the dissolution, the diffusion of Cu could proceed and the reacted structure shown in Fig. 4 was formed.

The samples contain a significant amount of oxygen as shown by the SIMS measurements. Results from the as-deposited Si/Ta(10 nm)/Cu(100 nm) sample are shown in Fig. 5. The intensity of oxygen is highest near the Ta/Cu interface as expected owing to the nature of the sputtering process. There is also a clear $^{16}O^{1}H^{-}$ peak at the same location indicating the presence of OH groups. It is evident that at the higher temperatures these groups will act as an additional source of oxygen. Moreover, there is a clear peak in the $^{181}Ta^{16}O$ molecular ion signal at the Ta/Cu interface (i.e., before the ^{181}Ta peak starts to rise), thus suggesting that Ta–O chemical bonds have formed. SIMS measurements of the as-deposited Si/Ta(50 nm)/Cu(100 nm) samples show similar behavior. At the Ta/Cu interface peaks in the ^{16}O, $^{16}O^{1}H^{-}$, and $^{181}Ta^{16}O$ molecular ion signals can be detected. There is also some oxygen at the Si/Ta interface (Fig. 6). Hence, it is evident that, despite the layer thicknesses, the as-deposited samples contain relatively large amounts of oxygen and that there is chemical bonding between Ta and O atoms at the Ta/Cu interface, indicating the existence of TaO_x layer. SIMS measurements of the 10-nm Ta layers annealed at 450 °C (Fig. 7) show that there are still significant amounts of oxygen in the films after the annealing. The $^{181}Ta^{16}O$ molecular ion

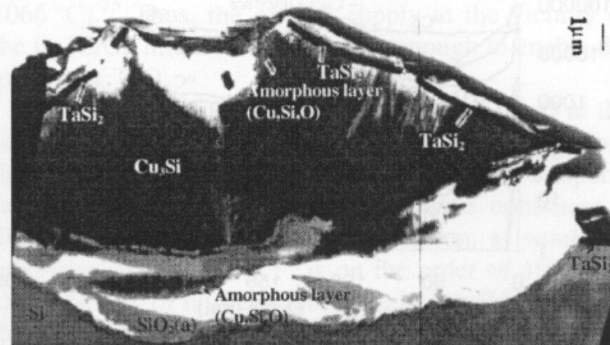

FIG. 4. Bright-field TEM image from the Si/Ta(100 nm)/Cu(400 nm) sample annealed at 685 °C for 30 min.

signal displays a peak at the Ta/Cu interface similar to the peak in the as-deposited samples. The intensity distributions of oxygen and Ta–O have already started to spread, indicating that the dissolution process has started. On the other hand, because SIMS can detect the $^{181}Ta^{16}O$ molecular ion signal at the interface still after the "low-temperature" annealings, it points out that the TaO_x layer is relatively stable. The increase in the intensity of oxygen inside the Ta layer seen in Figs. 5–7 (after the ^{181}Ta peak has started to rise) is most likely a Ta matrix effect. The spectra also suggests that there could be some Cu inside the Si substrate. However, this can most probably be attributed to ion beam mixing at the layer interface, since Cu penetration was not observed with other analytical techniques at this temperature. For example, Au or Pt overlayer on Si sputtered with 20-keV Cs^+ ions can have the overlayer signal extended over 100 nm into the substrate.[18] The fact that there is a very thin (10 nm) Ta layer between Cu and Si is expected to reduce the effect but not to remove it entirely. Moreover, since chemical inhomogeneities in the mixed zone, particularly the presence of oxygen, strongly influence the mixing process by enhancing segregation effects, and therefore usually degrading depth resolution,[19] the results obtained from the SIMS analyses should be used cautiously. At still higher temperatures (in fact already at 500 °C) the SIMS spectra of the Si/Ta(10 nm)/Cu(100 nm) samples show that the distribution of oxygen in the layers start to spread significantly pointing out that the interfacial layer continues to dissolve. The process is expected to take place over a relatively wide temperature range. The SIMS results of the Si/Ta(50 nm)/Cu(100 nm) samples after annealing are similar to those of the Si/Ta(10 nm)/Cu(100 nm) samples, except for the higher temperature where the intensity distribution of oxygen starts to spread out. Therefore, it is safe to assume that also the thickest Si/Ta(100 nm)/Cu(400 nm) samples behave similarly, except for the higher temperatures where the oxide dissolution starts. All the samples, with or without annealing, also contain some carbon, but no trace of nitrogen can be detected. This is important from the thermodynamic point of view as discussed later on. In combination with the results from the TEM/EDS analyses, the results from the SIMS analyses provide considerable support to the suggested interfacial oxide layer between Cu and Ta in this system.

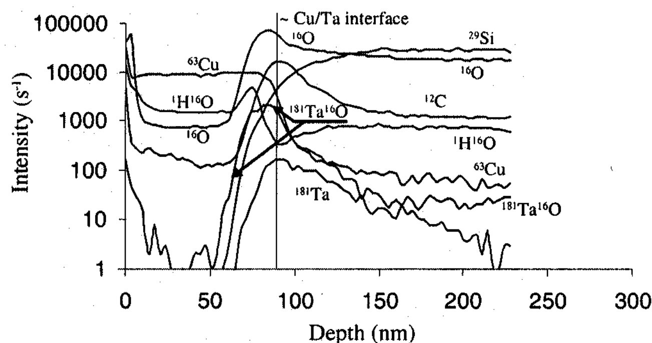

FIG. 5. Results from the SIMS analyses of the as-deposited Si/Ta(10 nm)/Cu(100 nm) sample. Approximated location of Cu/Ta interface is also indicated in the figure.

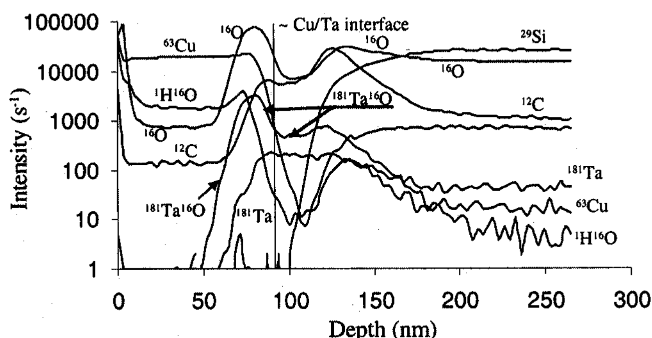

FIG. 6. Results from the SIMS analyses of the as-deposited Si/Ta(50 nm)/Cu(100 nm) sample. Approximated location of Cu/Ta interface is also indicated in the figure.

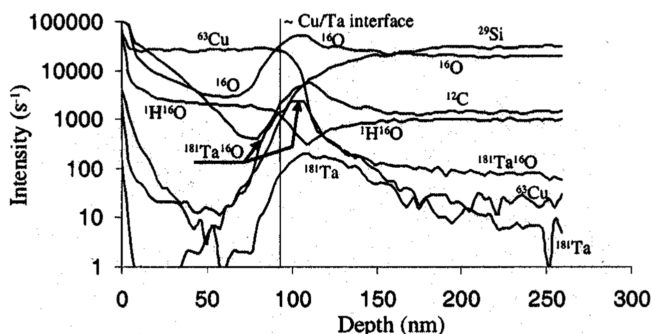

FIG. 7. Results from the SIMS analyses of the Si/Ta(10 nm)/Cu(100 nm) sample annealed at 450 °C for 30 min. Approximated location of Cu/Ta interface is also indicated in the figure.

To further investigate the effect of oxygen on the reactions in the metallization system, thermodynamic analysis of the binary Ta–O system was carried out. The thermodynamic descriptions of the stable bcc-$Ta[O]_{ss}$ solid solution and the stable oxide Ta_2O_5 were optimized using the experimental solubility data and the compiled thermodynamic data on the pure oxygen, the bcc-Ta, and the Ta_2O_5.[34–38] Since no thermodynamic data for the metastable β–Ta or metastable Ta oxides are available, the bcc-$Ta[O]_{ss}$ and the Ta_2O_5 phases are used throughout the analysis. The optimization procedure involved in performing thermodynamic description of the system is described elsewhere.[20,21]

It is argued that, during the deposition, some oxygen available in the sputtering atmosphere becomes entrapped in the growing β–Ta layer and, in particular, into numerous grain boundaries. The upper part of the β–Ta layer, i.e., near the β–Ta/Cu interface, should also contain higher amounts of oxygen than the underlying part of the film. This kind of oxygen pick up by tantalum

during sputtering under high vacuum has also been previously noticed.[9] Because of the low temperature (approximately 100 °C) during the sputtering, the dissolution of the entrapped oxygen from the grain boundaries into the β–Ta matrix is not kinetically favored. Therefore, a mixed layer containing Ta, O, and Ta–O chemical bonds is formed at the oxygen-rich β-Ta/Cu interface. The presence of oxygen as well as the Ta–O chemical bonding in the as-deposited samples was experimentally shown by the SIMS measurements. Thus, it is likely that a metastable amorphous TaO_x layer is formed at the interface and that it will transform into the stable tantalum oxide later on when enough thermal activation is provided.

To predict whether the amorphous TaO_x exists during the following annealings at higher temperatures, it is important to know also the solubility of TaO_x in β–$Ta[O]_{ss}$ under the annealing conditions. The solubility of the Ta_2O_5 in the bcc-$Ta[O]_{ss}$ solid solution is 1.4 at.% and that of the TaO_x in the bcc-$Ta[O]_{ss}$ approximately 4 at.% oxygen at 600 °C (Figs. 8 and 9), since the solubilities of metastable phases are larger than those of the stable phases (2–3 times).[22] Analogously, because the Gibbs energy curve of the β–Ta must lie above that of the bcc-Ta, the solubility of the TaO_x in β–$Ta[O]_{ss}$ is less than in the bcc-Ta. According to the experimental data, markedly lower external oxygen levels than used in the annealing environment can saturate the bcc-Ta matrix with respect to the Ta_2O_5 (and also TaO_x).[23] Thus, there is a very large oxygen potential driving the atmospheric oxygen to dissolve into the β–Ta lattice during the annealing. ($p_{O_2} \approx 10^{-4}$ Pa). This ensures that the entrapped

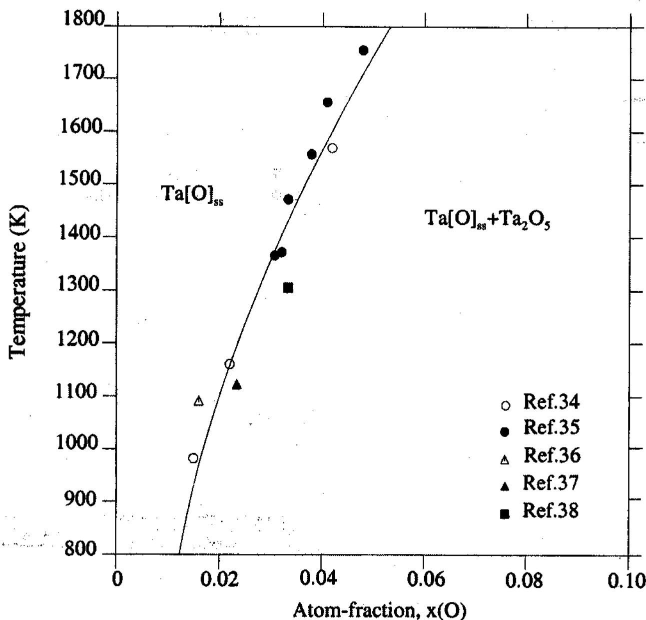

FIG. 8. Ta-rich part of the binary Ta–O phase diagram showing the evaluated solvus line in equilibrium with Ta_2O_5.

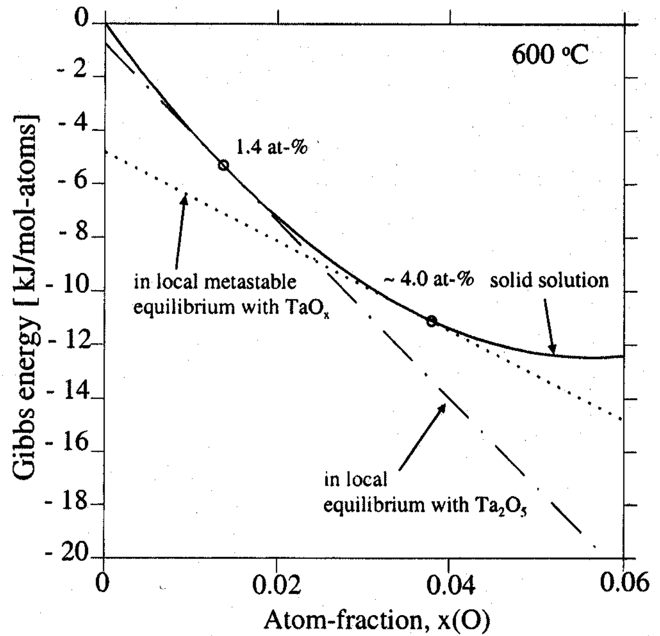

FIG. 9. Gibbs energy curve of the $Ta[O]_{ss}$ solid solution at 600 °C, showing the solubility of the Ta_2O_5 and the solubility of the TaO_x in the bcc-$Ta[O]_{ss}$ solid solution.

oxygen in the thin-film structures cannot escape through the Cu grain boundaries to the annealing atmosphere. Moreover, because the kinetics prevents the dissolution of the TaO_x into the β–Ta and because more oxygen from the atmosphere is penetrating into the films, TaO_x has to grow. The volume diffusion coefficient of oxygen in copper [$D_O^{Cu} \approx (1.7 - 2.1) \times 10^{-10}$ m²/s] at the temperature range of interest as calculated from the experimental data[23,24] shows that oxygen has significant penetration depth during the annealing. As the structure of the Cu overlayer is strongly columnar enablening grain boundary diffusion to take place, the above calculated value (D_O^{Cu}) can be taken as the lower limit for the diffusion coefficients. While some oxygen is also incorporated into the Cu matrix during the deposition, it will be repelled from the Cu matrix to the Ta/Cu interface during the annealing, due to the low solubility of oxygen into Cu matrix (maximum of 0.015 at.% at 1066 °C).[25] Thus, the oxygen supply at the vicinity of the β–Ta/Cu interface is more than enough to enable the growth of TaO_x.

It is to be noted that the formation of the Cu_2O at the sample surface is not possible under the annealing conditions (oxygen pressure of 0.2×10^{-4} Pa and temperature 600 °C).[16,27] and can not therefore constitute a diffusion barrier against oxygen diffusion, as would be otherwise expected ($D_O^{Cu_2O}$ is on the order of 10^{-19} m²/s).[26] The role of nitrogen must also be considered, since the external nitrogen pressure in the annealing atmosphere is approximately 0.8×10^{-4} Pa and, consequently, some nitrogen could also diffuse from the annealing

atmosphere into the thin film structure. However, according to the experimental data, the potential driving nitrogen to dissolve into the bcc-Ta under the annealing conditions is several orders of magnitude less than that of oxygen.[23] Moreover, since the experimental information from the SIMS measurements does not show any traces of nitrogen in the annealed films, nitrogen is excluded from the analysis.

The transformation of the TaO_x into the stable Ta_2O_5 will take place well below 600 °C (i.e., before the transition of the β–Ta to the bcc-Ta occurs).[28,29] Due to this transformation the metastable local equilibrium between the Ta_2O_5 and the β–Ta$[O]_{ss}$ is established. As the Ta_2O_5 solubility in the β–Ta$[O]_{ss}$ is less than in the bcc-Ta$[O]_{ss}$, the formation of the Ta_2O_5 also drives the structural transition to reach the stable local equilibrium (i.e., the local equilibrium between the bcc-Ta$[O]_{ss}$ and the Ta_2O_5). When the transition takes place a higher temperatures (above 600 °C),[28] the solubility of the Ta_2O_5 is increased. More importantly, the open structure of the stable bcc-Ta will enhance the interstitial diffusion of oxygen and thereby the rate of the dissolution of the interfacial oxide.

Figure 10 gives a schematic presentation of the proposed reaction sequence in the 100-nm-thick Ta films. The as-deposited samples contain relatively large amounts of oxygen and OH groups as indicated by the SIMS measurements. A composite layer of tantalum–oxygen is also detectable at the Ta/Cu interface after the deposition. During the annealings, further incorporation of oxygen into the samples take splace. Oxygen diffuses most probably via grain boundaries to the interface between Ta and Cu and becomes incorporated as the metastable oxide TaO_x, which will later transform into the stable Ta_2O_5. The presence of the TaO_x layer at higher temperatures is supported by the SIMS results, which shows clear signals of molecular $^{181}Ta^{16}O$ near the Ta/Cu interface (i.e., before the ^{181}Ta peak starts to rise). This interfacial oxide prevents the diffusion of Cu through the strongly columnar Ta layer until the oxide layer can be dissolved. Because of the kinetic constraints, the dissolution of the oxide is not possible until a certain threshold temperature range has been reached. Some evidence of the onset of the dissolution process can be seen in the SIMS profiles taken from the Si/Ta(10 nm)/Cu(100 nm) samples annealed at 450 °C, where the peaks of the ^{16}O and $^{181}Ta^{16}O$ molecular ion signals start to spread out. In the thicker (100-nm Ta) films the temperature region where the dissolution starts is expected to be higher (>600 °C). Dissolution of the interfacial oxide can be thought of as a two-step process. The first step is the dissociation of the oxide. This is expected to proceed by generating vacancies of the type V_O^{2-}.[30] In this process, mobile neutral oxygen atoms are produced across the whole Ta_2O_5 layer. The second step is the transportation of neutral oxygen atoms into the tantalum matrix. From the literature[31] it can be found that the diffusion coefficient of oxygen in the bcc-Ta is 5 orders of magnitude larger than in the Ta_2O_5. This will enable fast diffusion of oxygen atoms from the bcc-Ta/Ta_2O_5 interface into the Ta matrix. The lack of extensive Cu diffusion up to 650 °C, as confirmed by EDS in combination with the SIMS results, provides strong experimental evidence of the presence of an interfacail oxide at the Ta/Cu interface. At sufficiently high temperatures a continuous $TaSi_2$ layer is formed. This layer becomes fractured by

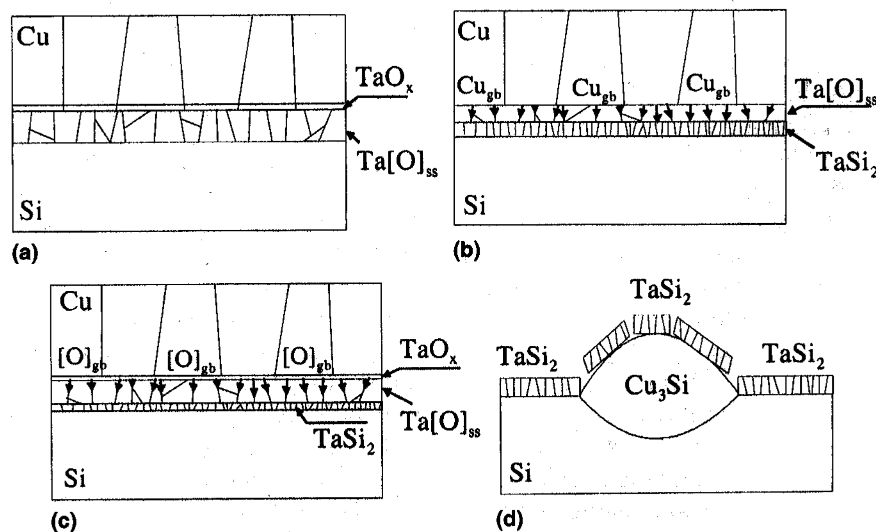

FIG. 10. Schematic presentation of the proposed reaction sequence in the Si/Ta(100 nm)/Cu(400 nm) samples: (a) as-deposited structure; (b) interfacial oxide starts to dissolve (>600 °C); (c) Cu diffusion through Ta and $TaSi_2$ (approximately 650 °C); (d) formation of the final reacted structure (approximately 685 °C).

the growth of large Cu_3Si protrusions initially located under the $TaSi_2$ layer. This mechanism leads to the structure seen in Fig. 4. The details of the reaction mechanism are presented in the earlier publication.[10]

With small Ta layer thicknesses, the high defect and grain boundary densities enable significant diffusion of Cu, despite the presence of the thin interfacial oxide layer. Moreover, the thinnest Ta films are likely to be under a high compressive stress,[32] which will further enhance the diffusion of all the species in the metallization system. This leads to a sequence where the Cu_3Si is the first phase to form followed by the formation of the $TaSi_2$, provided that the temperature is high enough (e.g., 600 °C or higher).[10] The formation of the $TaSi_2$ is controlled by the diffusion of Si, which requires the release of Si atoms from the Si lattice and thereby relatively high temperature.[33] The effect of the growing $TaSi_2$ on the dissolution of the interfacial oxide is not clear at the moment. It is known, however, that, during the oxidation of the $TaSi_2$, both the Ta_2O_5 and the SiO_2 are formed. In addition, the Ta_2O_5 has been observed to decompose when grown on top of the $TaSi_2$.[29] Therefore, we cannot exclude the possible role of the $TaSi_2$ layer, even though we consider it to be less important than the formation of the $Ta[O]_{ss}$ solid solution. It should be emphasized that due to the numerous factors influencing the reactions the determination of exact reaction mechanisms taking place in the metallization structures with the thin Ta layers need further experimental and theoretical studies.

IV. CONCLUSIONS

We have found that oxygen plays a major role in the reactions occurring in the Si/Ta/Cu metallization system. There is experimental evidence that an interfacial oxide layer is formed between Cu and Ta. This oxide is the metastable TaO_x, which will ultimately transform into the stable Ta_2O_5. By constituting an additional barrier layer, the metastable oxide retards the diffusion of Cu up to much higher temperatures than is expected on the basis of the microstructure of the thin films. Practically no traces of Cu were observed inside the Ta layer up to 650 °C with the TEM/EDS analyses, thus giving experimental support to the assumption of the existence of an additional film between Ta and Cu. The SIMS analyses indicated clearly that Cu and Ta films contained significant amounts of oxygen already as-deposited and that the oxygen distribution profile displayed a peak near the Ta/Cu interface. The spreading of the SIMS oxygen profiles after high-temperature annealing denotes the onset of the dissolution of the interfacial oxide layer. Only after the oxygen is released and incorporated into the Ta matrix can the diffusion of Cu proceed. The dissolution of the oxide layer is thermodynamically possible in a wide temperature range, as confirmed by the thermodynamic analysis of the Ta–O system. Therefore, it is the kinetics of the oxygen dissolution that determines the temperature region where the Ta barrier ultimately fails. It was also found that the threshold temperature range for the dissolution coincided with that of the β–Ta to the bcc-Ta transition, which is expected to enhance the kinetics. The effects of the microstructure and of the film stresses on copper and oxygen diffusion appear to be more pronounced when the Ta film thickness is reduced. Hence, the stability of a Ta diffusion barrier between Cu and Si is crucially dependent on oxygen available for the formation of the thin oxide layer at the Ta/Cu interface.

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