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Failure mechanism of Ta diffusion barrier between Cu and Si

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The reaction mechanisms in the Si/Ta/Cu metallization system and their relation to the microstructure of thin films are discussed on the basis of experimental results and the assessment of the ternary Si–Ta–Cu phase diagram at 700 °C. With the help of sheet resistance measurements, Rutherford backscattering spectroscopy, x-ray diffraction, a scanning electron microscope, and a transmission electron microscope, the Ta barrier layer was observed to fail at temperatures above 650 °C due to the formation of $TaSi_2$, the diffusion of Cu through the silicide layer, and the resulting formation of Cu_3Si precipitates. However, in order for the $TaSi_2$ phase to form first, the Ta diffusion barrier layer must be thick enough (e.g., 50–100 nm) to prevent Cu diffusion into the Si substrate up to the temperature of $TaSi_2$ formation (~650 °C). Independent of the Ta layer thickness, Cu_3Si was present as large nodules, whereas the $TaSi_2$ existed as a uniform layer. The resulting reaction structure was found to be in local equilibrium on the basis of the assessed Si–Ta–Cu phase diagram at 700 °C, and therefore no further reactions were expected. The role of oxygen was also found to be important in the reactions and it seems to have a strong effect on the thermal stability of the barrier layer. © *2000 American Institute of Physics.*
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I. INTRODUCTION

The continuing demand to improve the performance of integrated circuits has lead to the need to replace aluminum conductors with materials that possess better electrical properties. Moreover, the reliability of aluminum conductors is limited by their relatively poor electromigration resistance. The material selected for the new conductor metal in integrated circuits is copper due to its better electrical properties as well as better electromigration resistance in comparison to aluminum.[1,2] Unfortunately, the interaction between Si and Cu is strong and detrimental to the electrical performance of Si even at temperatures below 200 °C.[3–6] Thus, it is necessary to implement a barrier layer between Si and Cu. From the diffusion barrier point of view tantalum has many good properties. It has a high melting point (3020 °C) and therefore is expected to have high activation energy for both lattice and grain boundary diffusion. It does not form intermetallic compounds with copper, thus providing a relatively stable interface between copper and tantalum. The reaction between silicon and tantalum is also known to require rather high temperatures (650 °C),[7] which in effect provide a reasonably stable Si/Ta interface. In addition, tantalum forms a stable oxide (Ta_2O_5), which provides a protective layer against copper corrosion and improves adhesion to SiO_2. It has been experimentally verified that tantalum protects the underlying copper from oxidation until a tantalum layer has been completely transformed into Ta_2O_5.[8]

Hence, it is not surprising that tantalum and its compounds have been suggested as a feasible diffusion barrier in copper-based metallization schemes by a number of authors.[8–15] The results and their interpretations are, however, quite contradictory. No general agreement concerning the reactions in the Si/Ta/Cu system has been achieved.

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. As a first approximation, copper is expected to be the moving species at this interface due to its much lower melting point in comparison to that of tantalum.[16] However, it is still possible for Ta to diffuse outwards, due to its high affinity towards oxygen, if there is enough available in the ambient. In addition, in a recent publication amorphous layer formation was found to take place between Cu and β-Ta thin films (thicknesses of 20 nm of Cu and 13 nm of Ta) by interdiffusion between Ta and Cu.[17] It was related to the transformation of β-Ta to α-Ta, which took place between 500 and 800 °C. It seemed that Ta was the main moving species during this reaction and Cu just offered short-circuit diffusion paths for the Ta phase transition. During the phase transition, the β-Ta film was broken at some locations and the α-Ta grains grew inside the Cu layer. This factor may cause problems with very small Ta diffusion barrier thicknesses (~10 nm). Thus, despite the faster lattice diffusion of Cu compared with Ta, it is not necessary for Cu to move first at this interface. Nevertheless, eventually Cu will start to penetrate through the Ta layer towards the Si substrate due to its high affinity with Si. The penetration time is a function of the Ta layer thickness, microstructure of the layer, annealing temperature, and interfacial and other physical properties.

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At the Ta/Si interface, the formation of $TaSi_2$ and Cu_3Si take place at temperatures around 630 °C according to previous investigations.[9,10] However, there is no general agreement about the reaction sequence. Holloway and Fryer[9] stated earlier that the formation of Cu_3Si took place together with the $TaSi_2$ formation. In a later publication[10] Holloway *et al.* stated that the Cu_3Si was formed first and only after that did $TaSi_2$ appear at a slightly higher temperature. Clevenger *et al.*[15] agreed with Holloway *et al.*,[10] stating that there was no evidence of $TaSi_2$ before Cu_3Si formation. Kang *et al.*,[12] on the other hand, take the opposite point. They stated that $TaSi_2$ was formed first and only after that did Cu manage to penetrate through the remaining Ta layer to react with silicon and form Cu_3Si. A similar view was also presented by Yoon *et al.*[14]

In the present study the reactions in the Si/Ta/Cu metallization system are investigated by utilizing a combined thermodynamic and kinetic approach. The phase relations in the system are examined with the help of the calculated ternary phase diagram. The information extracted from these diagrams is coupled with the experimental results obtained to reveal the underlying mechanism(s) leading to the failure. It is believed that with this approach it is possible to achieve more profound insight into the equilibria and the reactions in the system.

II. MATERIALS AND METHODS

The copper and tantalum films were sputtered onto cleaned and oxide-stripped (100) oriented *n*-type Si substrates in a dc/rf-magnetron sputtering system. The thickness of the tantalum layer was about 100 nm. The structure of the Ta layer was determined to be metastable tetragonal β-Ta by x-ray diffraction. The copper film, with a thickness of 400 nm, was subsequently sputtered onto this film without breaking the vacuum. The base pressure for the deposition runs was 3×10^{-5} Pa. In order to investigate the effect of the barrier thickness on the thermal stability of the metallization structure, some additional samples with thinner tantalum (10 and 50 nm) and copper layers (100 nm) were fabricated. The experimental results presented below are from the Si/Ta (100 nm)/Cu (400 nm) samples, unless otherwise stated. The samples were annealed in a vacuum of 10^{-4} Pa or better at temperatures ranging from 500 to 800 °C for 30 min.

Sheet resistance measurements at room temperature using a four-point probe were used to detect interfacial reactions after each annealing step. The reaction products in the Si/Ta/Cu metallization scheme were characterized by x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and transmission electron microscopy (TEM). XRD analysis was conducted with a Seifert XRD 3000 TT vertical $\theta-\theta$ diffractometer with 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 operated at 200 kV. Surfaces of the samples were also examined with an optical microscope and a scanning electron microscope (SEM). The results of the investigations were compared with the calculated phase diagram.

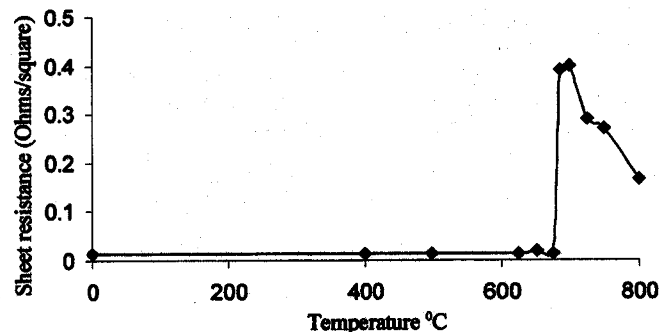

FIG. 1. Sheet resistance vs temperature curve of the Si/Ta (100 nm)/Cu (400 nm) structure annealed at different temperatures.

Calculation of the ternary Si–Ta–Cu phase diagram was extrapolated from the assessed binary thermodynamic data. A phase diagram is used to obtain information about the phases that can exist in equilibrium at given temperatures. Furthermore, if the diagram is coupled with available kinetic information, it is possible to predict phase formation and the phase formation sequence in diffusion couples. However, these kinds of predictions must be done with caution for the thin film systems, since using phase diagrams to predict the phase formation sequence entails the assumption that local equilibrium is attained at the interfaces, which may not be the case in a thin film system. The assumption of local equilibrium requires that reactions at the interfaces be fast enough to use all the atoms arriving in the reaction region immediately and that the rate-determining step is diffusion. However, with very thin layers this requirement may not be fulfilled. The reasons for this originate mainly from special conditions prevailing during thin film reactions: (a) relatively low reaction temperatures, (b) small dimensions, (c) the high density of short-circuit diffusion paths, (d) relatively large stresses incorporated in thin films, (e) the relatively high concentration of impurities, (f) metastable structures, (g) large gradients, and so on. However, despite the difficulties mentioned, it is expected that it is easier to understand the behavior of the metallization system with the help of the equilibrium diagram.

III. RESULTS AND DISCUSSION

The sheet resistance as a function of temperature is shown in Fig. 1. At a temperature of 625 °C, there is a slight increase in the sheet resistance. At 685 °C there is an abrupt rise in the curve indicating that a reaction(s) has occurred in the system. Above 700 °C the sheet resistance starts to decrease, and the structure behaves as an intrinsic semiconductor. Thus, the underlying silicon is now carrying almost all the probe current. This behavior is similar to that observed in previous investigations.[9,10] Samples with thinner Ta layers showed identical behavior except for the lower failure temperatures. The failure temperatures were 600 and 550 °C for the 50 and 10 nm Ta layers, respectively. These findings indicate that the thermal stability of thin Ta layers may not be adequate for practical devices. However, it must be realized that the sheet resistance measurements monitor mainly the state of the Cu overlayer, since it carries almost all the

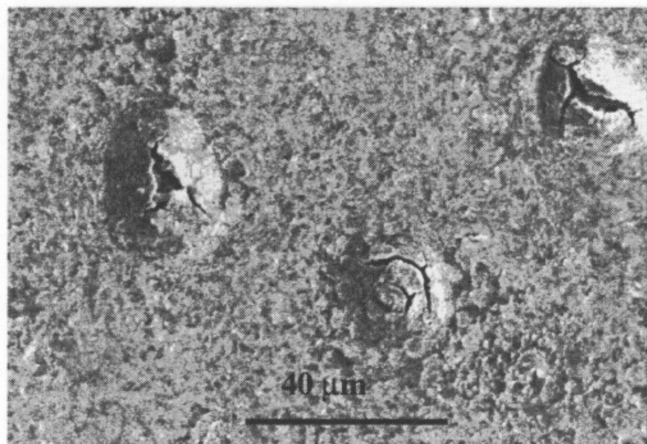

FIG. 2. SEM image from the surface of the Si/Ta (100 nm)/Cu (400 nm) sample annealed at 685 °C for 30 min.

probe current. Hence, the interaction between other layers, e.g., Ta and Si, may not be immediately detected. The surfaces of the samples maintained a shiny copper-like appearance up to 675 °C. However, at this temperature and even at 625 °C, there were small spot-like defects indicating that reaction(s) could have been initiated. The samples annealed at 685 °C had already completely lost their metallic copper appearance and their color appeared to be a hazy silver. The SEM picture of the surface structure of the sample annealed at 685 °C is shown in Fig. 2. As can be seen, large "bumps" appear at the surface. The size of the defects is quite large, about 20–30 μm in diameter.

The RBS measurements were conducted in order to obtain more information on the reactions (Fig. 3). The discrete layers of Ta and Cu are clearly seen in the spectrum from the samples without annealing. The measurements showed that these layers were present up to 675 °C without evidence of severe intermixing. At 625 °C [Fig. 3(b)] there is a shift in the Ta peak towards the surface, but it can be attributed to the thickness variations in the Cu layer as the trailing edge of the Cu peak also shifts about the same amount. The occurrence of the small surface peak corresponding to that of Ta indicates that a small amount of tantalum has diffused to the surface of the sample, impurity of the sputtering target is reflected in the fact that the Nb surface peak is also detected at 625 and 675 °C [Figs. 3(b) and 3(c)]. This behavior is similar to that previous investigations.[9,10] Diffusion of Ta may occur if there is enough oxygen in the vacuum system, since Ta has a very high affinity towards oxygen. It is also possible that stresses incorporated into the Ta film during deposition enhance the diffusion of Ta. Previous experiments have shown that a potential gradient of force gives rise to a mean diffusion velocity for the affected atoms.[18] We found the structure of the Cu layer to be columnar (see Fig. 7), thus providing short-circuit paths for Ta diffusion. This columnar structure also enables oxygen diffusion from the atmosphere through the Cu layer to the Ta/Cu interface. This may play a significant role in the reactions taking place at the higher temperatures. At 625 °C [Fig. 3(b)] there seems to have been some interdiffusion of Ta and Si, since the slopes of the trailing edge of the Ta and the leading edge of the Si signals

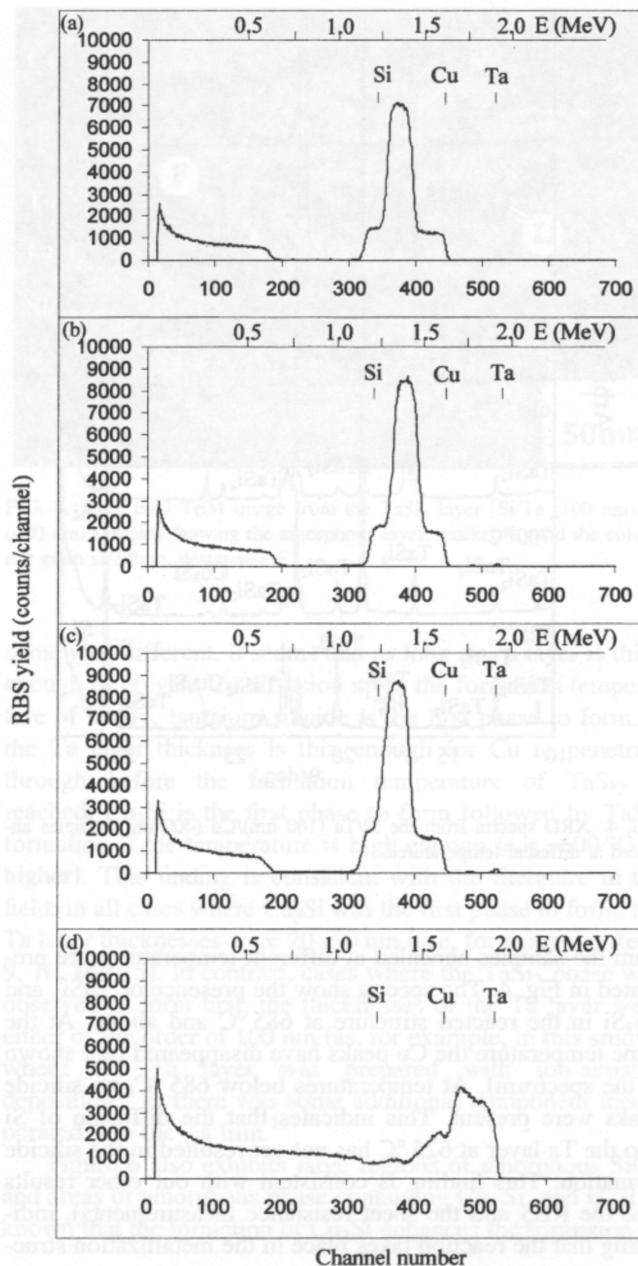

FIG. 3. RBS spectra (2.0 MeV 4 He^+, θ=170°) from the Si/Ta (100 nm)/Cu (400 nm) samples with (a) no annealing and (b) annealed at 625, (c) 675, and (d) 685 °C. Vertical arrows represent surface scattering energies of the marked elements.

have smoothened. Hence, the RBS measurements indicate the formation of a mixed Ta–Si layer. It is probable that Si has diffused into the Ta layer, since it has been determined to be the moving species during the formation of $TaSi_2$.[7] Possible silicide formation is further discussed below with the XRD and TEM results. At 685 °C the spectrum shows that the reaction(s) have led to catastrophic failure of the Ta–Cu thin film structure. The spectrum at this temperature is quite complicated and a detailed interpretation would be difficult. Figure 2 helps to exemplify this. As the surface does not stay planar, the interpretation of the RBS spectrum is not unambiguous.

XRD analyses were conducted in order to reveal the phase formation during the reaction at 685 °C. The results

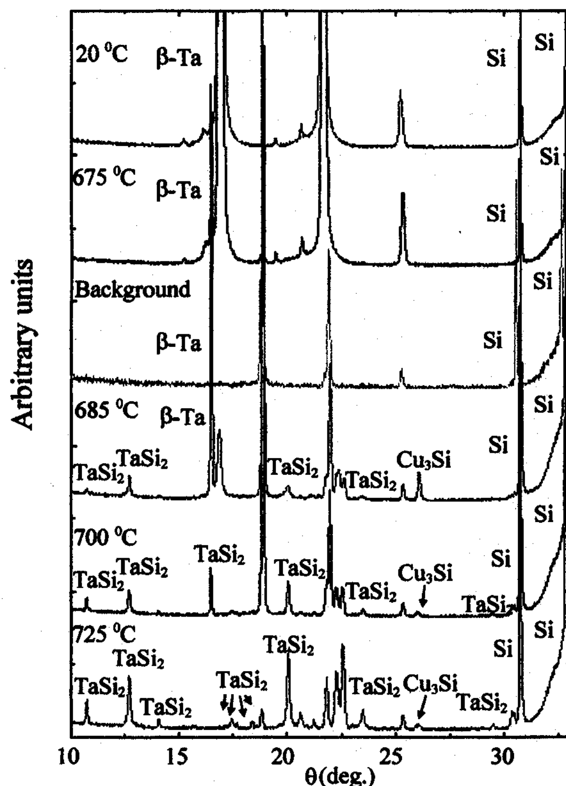

FIG. 4. XRD spectra from the Si/Ta (100 nm)/Cu (400 nm) samples annealed at different temperatures.

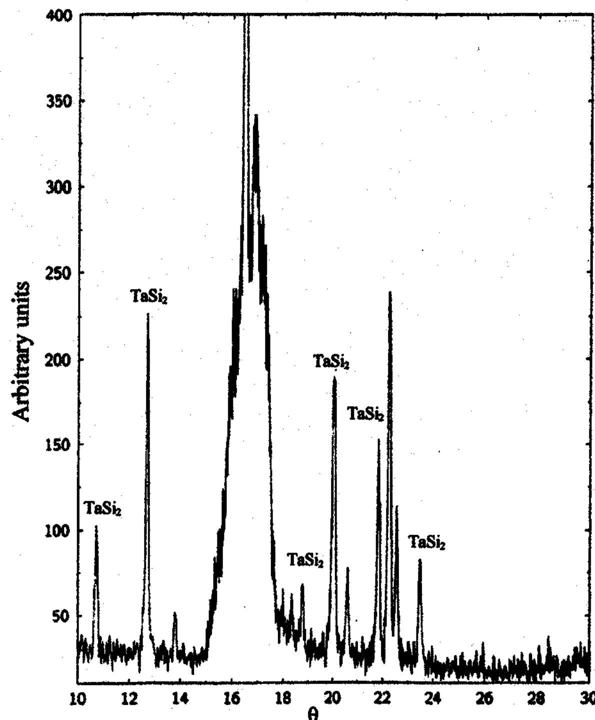

FIG. 5. XRD spectra from the Si/Ta (50 nm)/Cu (100 nm) sample annealed at 600 °C showing the formation of $TaSi_2$ in the sample.

from the samples annealed at different temperatures are presented in Fig. 4. The spectra show the presence of $TaSi_2$ and Cu_3Si in the reacted structure at 685 °C and above. At the same temperature the Cu peaks have disappeared (not shown in the spectrum). At temperatures below 685 °C, no silicide peaks were present. This indicates that the diffusion of Si into the Ta layer at 625 °C has not yet resulted in the silicide formation. This finding is consistent with our other results (see the RBS and the sheet resistance measurements), indicating that the reaction takes place in the metallization structure very abruptly. No new phases occur at higher temperatures, indicating that the structure is an equilibrium one. Some changes in the intensities of the diffraction lines can be observed, but this is because the reaction has not been completed at 685 °C, as is also indicated by the RBS spectrum at the same temperature. Nevertheless, it must be emphasized that the resolution of conventional XRD may not be high enough to detect very thin silicide phases which may have formed at temperatures below 685 °C. For example, the formation of $TaSi_2$ is expected at 650 °C.[7]

The structures of the thin samples with 50 and 10 nm thick Ta layers were different after annealing at 600 and 550 °C, respectively. For the 50 nm sample annealed at 600 °C, the reacted structure also consisted of Si–Cu_3Si–$TaSi_2$ (Fig. 5), but with the 10 nm sample annealed at 550 °C, the structure was Si–Cu_3Si–Ta and no trace of $TaSi_2$ was detected as expected.[15] The fact that $TaSi_2$ was present at 600 °C suggests that Cu must somehow facilitate the Ta-silicide formation, which is not expected below 650 °C. The mechanism for lowering of the $TaSi_2$ formation temperature is explained as follows. Copper atoms penetrate through the thin Ta layer along the grain boundaries and defects. When they reach the Si/Ta interface the nucleation of Cu_3Si takes place. This nucleation and the "in-diffusion" of Cu into the Si substrate are believed to enhance the $TaSi_2$ formation. It is suggested in the literature that the formation rate of $TaSi_2$ is mainly governed by the release rate of Si atoms from the lattice.[19] Since copper has been observed to diffuse interstitially in Si,[3] it is probable that when Cu atoms penetrate the Si lattice their presence in interstitial sites decreases the Si–Si bond strength nearby, thus making it easier to release Si atoms from the lattice. For the 10 nm Ta layers, the temperature after the Cu_3Si formation (550 °C according to the XRD and sheet resistance measurements) is too low for $TaSi_2$ to form even with the assistance of Cu. The enhancing effect of the Cu overlayer on $TaSi_2$ formation has also been detected in other investigations.[9,10]

In order to examine the reaction sequence and the resulting morphology in detail cross-sectional TEM (XTEM) investigations were conducted. The cross-sectional view from the sample annealed at 685 °C is presented in Fig. 6. At the center of Fig. 6 there is a large nodule, which extends into the underlying substrate to a significant depth, determined by the position lying immediately to the side of the nodule. The composition of the "bulk" nodule was confirmed to be Cu_3Si with diffraction patterns obtained from the TEM investigations. The existence of $TaSi_2$ as a uniform layer was also confirmed. In Fig. 6 one can see that the uniform $TaSi_2$ layer is broken at the edges of the Cu_3Si nodule and continues on top of the nodule. This clearly indicates that a continuous $TaSi_2$ layer was present before the Cu_3Si "precipi-

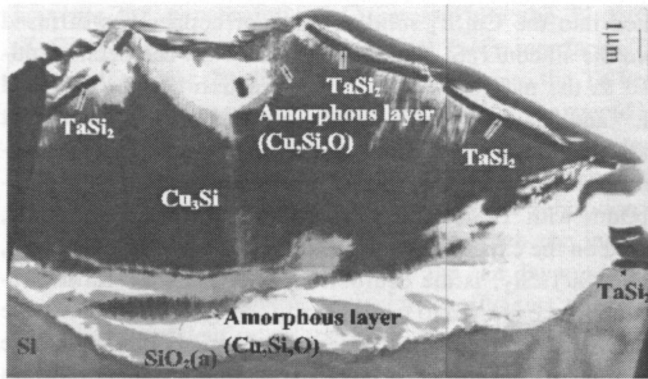

FIG. 6. Bright field TEM image from the Si/Ta (100 nm)/Cu (400 nm) sample annealed at 685 °C for 30 min.

tates'' started to grow. Further evidence of this can be seen in Fig. 7 where XTEM results from the sample annealed at 650 °C are presented. Figure 7 displays a crystalline layer with thickness locally as high as 85 nm between the Ta layer and Si substrate. This layer was identified as $TaSi_2$. In addition to this layer, there is a very thin amorphous layer between $TaSi_2$ and Si marked by L in Fig. 8. This is believed to be an amorphous Ta–Si layer. Previous research shows that amorphous layer formation takes place between Ta and Si at temperatures below 600 °C and that the layer can coexist with the crystalline $TaSi_2$ up to 700 °C.[17,20] The structure of the $TaSi_2$ layer is columnar as seen in Figs. 8 and 9. Since the microstructure of the Ta layer was also determined as columnar,[21] the morphology of the $TaSi_2$ layer in Figs. 8 and 9 is not surprising. This columnar structure offers many short-circuit diffusion paths through which Cu can penetrate to the Si substrate. The diffusion of Cu would lead to the formation of Cu_3Si precipitates and their further growth would result into the structure in Fig. 6.

It can be concluded that the first phase to form is $TaSi_2$. However, it must also be emphasized that this may not be the case with thin Ta layers, since their failure temperatures are below the required formation temperature of $TaSi_2$. This observation indicates that the failure mechanisms of thick (order of 100 nm) and thin (order of 10–50 nm) layers are

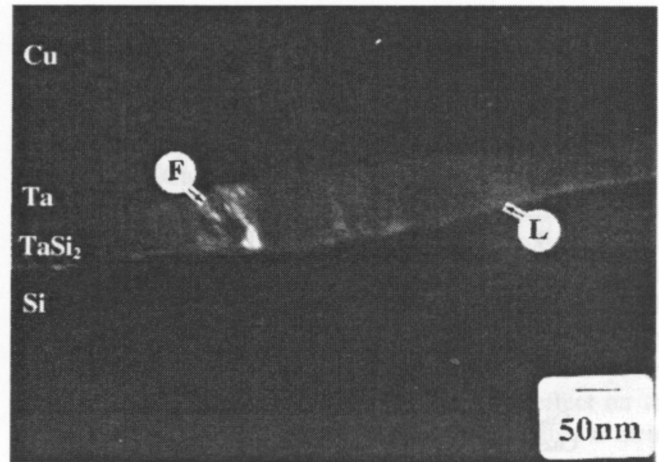

FIG. 8. Dark field TEM image from the $TaSi_2$ layer [Si/Ta (100 nm)/Cu (400 nm) sample] showing the amorphous layer, marked L, and the columnar grain structure, designated F.

somewhat different. It seems that as long as Ta layer is thick enough to prevent Cu diffusion up to the formation temperature of $TaSi_2$, tantalum silicide is the first phase to form. If the Ta layer thickness is thin enough for Cu to penetrate through before the formation temperature of $TaSi_2$ is reached, Cu_3Si is the first phase to form followed by $TaSi_2$ formation if the temperature is high enough (e.g., 600 °C or higher). This finding is consistent with the literature in the field: in all cases where Cu_3Si was the first phase to form, the Ta layer thicknesses were 20–50 nm (see, for example, Refs. 9, 10, and 15). In contrast, cases where the $TaSi_2$ phase was observed to form first, the thicknesses of the Ta layer were either of the order of 100 nm (as, for example, in this study), where the Ta layer was prepared with ion-assisted deposition[12] or there was some additional component incorporated into the Ta film.[14]

Figure 6 also exhibits large regions of amorphous SiO_2 and areas of amorphous phase containing Cu, Si, and O. It is known that the formation of Cu_3Si enhances the formation of

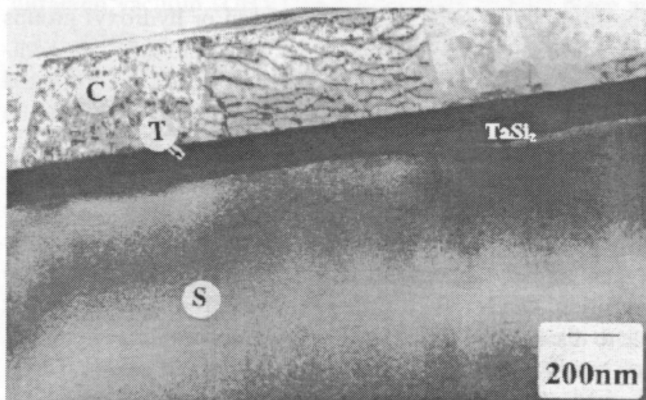

FIG. 7. Bright field TEM image from the Si/Ta (100 nm)/Cu (400 nm) sample annealed at 650 °C showing the formation of $TaSi_2$. C is the copper layer, T is the tantalum layer, and S is the Si substrate.

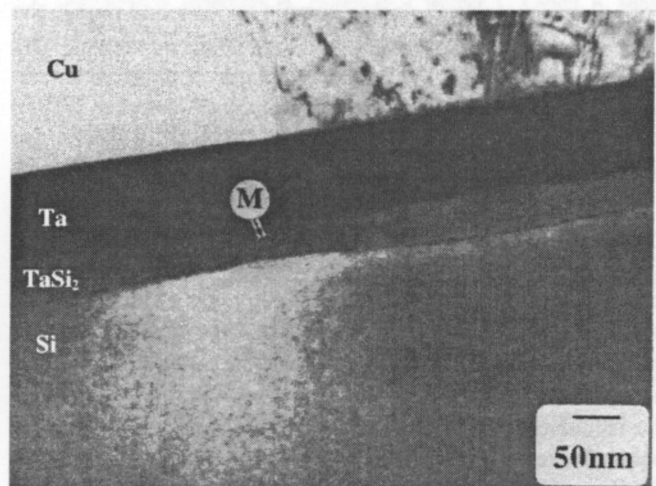

FIG. 9. Bright field TEM image from the Si/Ta (100 nm)/Cu (400 nm) sample annealed at 650 °C showing the columnar grain structure, designated M.

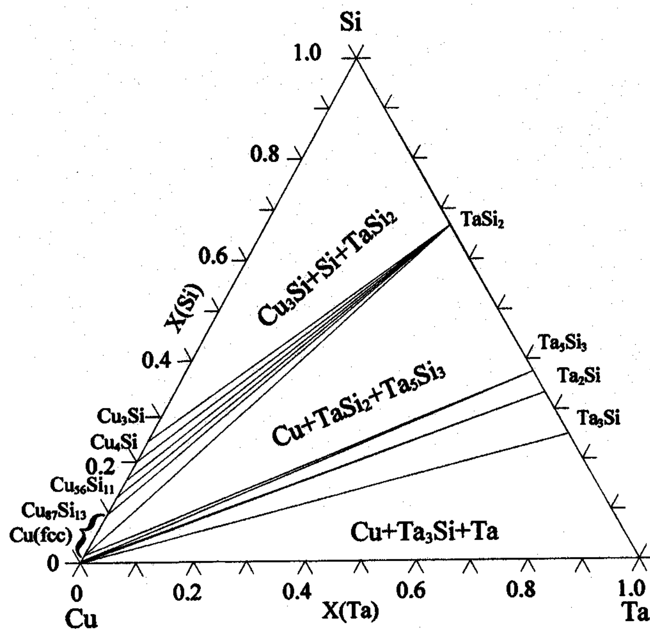

FIG. 10. Isothermal section from the calculated ternary Si–Ta–Cu phase diagram at 700 °C.

SiO_2,[22] thus the presence of oxides in the sample is not surprising. This oxide formation has taken place after the rupture of the $TaSi_2$ layer. There are also large holes beneath the Cu_3Si nodule (Fig. 6), indicating that considerable stresses have been generated during the formation of this structure. Some of these holes have probably formed during sample preparation but large stresses are expected to develop during the reaction. It is known that the formation of Cu_3Si in silicon is associated with a large volume expansion of 150% per Cu atom in Si,[23] leading to stress relaxation and production of intrinsic point defects. Furthermore, stresses are expected to evolve during sample cooling due to the large mismatches in (the coefficients of thermal expansion) (CTEs) among the different phases. This also provides an alternative explanation to the observed structure, since the $TaSi_2$ layer may break during sample cooling and enable the Cu to react directly with the Si. There would be enough time for the formation of Cu_3Si during sample cooling, since the sample stayed above room temperature at least for 20–30 min. It is known that the formation of Cu_3Si takes place even at temperatures around 150 °C.[24]

In order to achieve a better understanding of the thin film system, the ternary Ta–Si–Cu phase diagram was calculated using the assessed binary thermodynamic data.[25–27] Possible ternary compounds have been excluded due to the short annealing times. In addition, the dissolution of a third element into binary silicides has been neglected because no experimental data are available. An isothermal section at 700 °C of the calculated diagram is shown in Fig. 10. The $TaSi_2$ is the only tantalum silicide which can exist in equilibrium with Cu_3Si and Si. Based on the phase diagram, there is also equilibrium among $TaSi_2$, Cu, and Si. The $TaSi_2$ is thermodynamically stable when in contact with Si and Cu until a sufficient amount of silicon (~10 at. %) has been incorporated into the Cu[Si] solid solution or copper has diffused into the silicon/$TaSi_2$ interface. Because Cu has been identified as the moving species in the reaction between Cu and Si,[28] and has a very high affinity towards Si, it is likely that the diffusion of Cu through the silicide layer is the mechanism which brings the copper silicide(s) (Cu_3Si) into equilibrium with $TaSi_2$. The diagram supports the assumption, based on the experimental results, that the resulting structure, Si/Cu_3Si/$TaSi_2$, is the equilibrium one. Thus, no further reactions are expected to take place in the system, and only the relative amounts of the phases can change. In the sample with the 10 nm thick Ta layer the resulting nonequilibrium Si/Cu_3Si/Ta structure is a result of kinetic constraints, e.g., nucleation and growth of $TaSi_2$ are inhibited due to the low reaction temperature.

The columnar grain structure of the Ta layer should facilitate fast diffusion of Cu into the Si substrate. However, the diffusion of Cu and the formation of Cu_3Si was retarded up to the temperature of formation of $TaSi_2$ (~650 °C). A probable reason for this is the above-mentioned polymorphic transformation of Ta, which impedes Cu diffusion up to higher temperatures due to the associated amorphous phase formation at the Ta/Cu interface. Nevertheless, a more probable reason for the elevated Cu diffusion temperature is the presence of an interfacial oxide. Tantalum has a very high affinity to oxygen. It forms one stable oxide, Ta_2O_5, together with several metastable oxides. In addition, the solubility of oxygen in the body-centered-cubic (bcc) lattice of Ta is high (~5 at. % at 1500 °C).[29] The presence of oxygen in the Ta layers is indicated indirectly by the formation of metastable β-Ta which is a bcc-based superlattice structure with only slight tetragonal distortion.[30] Despite the fact that it is not clear whether β-Ta is stabilized by impurities or not,[31] we suggest that the mechanism for the polymorphic transformation is the dissolved oxygen in the octahedral sites of the bcc lattice. This would lead to the tetragonal structure with the c/a ratio smaller than 1, as has been previously observed.[31,32] 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 metastable oxide, TaO_x, and eventually to the formation of the bcc Ta.[32] It is also reported that the metastable tetragonal TaO_2 layer forms immediately at the substrate/film interface at the beginning of deposition when there are either oxygen or hydroxyl groups present which act as a template for β-Ta growth.[33] In addition, it is evident that some oxygen has been incorporated into the Ta layer from the annealing environment. Since the Cu overlayer was observed to have a columnar microstructure, the short-circuit diffusion of oxygen into the Ta/Cu interface is expected to occur in a reasonable time scale. 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 thin metastable oxide layer is formed at the Ta/Cu interface.

Thus, we anticipate that the formation of metastable tantalum oxide (TaO_x) is the reason for the retarded diffusion of the Cu atoms. Below 650 °C the presence of the oxide layer

prevents the penetration of Cu atoms into the Si lattice ($Ta/TaO_x/Cu$ "system" at the original Ta/Cu interface). The driving force for the dissolution of oxygen into the Ta layer is very high.[29] Hence, the Ta–O solid solution is expected to be more stable than the oxide layer (Ta_2O_5) in a large temperature range. However, the dissolution of oxygen into the Ta-rich layer becomes possible only after the relaxation of kinetic constraints. This 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 kinetics of the dissolution reaction change strongly with temperature. Thus, it is suggested that at temperatures below 650 °C kinetic constraints prevent the dissolution of the oxide layer which is impeding the migration of Cu atoms. Only after the "threshold" temperature is reached can the dissolution of the oxide layer proceed so that Cu atoms are able to diffuse into the Si lattice and the reactions can take place between Cu and Si at the Si/$TaSi_2$ interface. In thin Ta layers (10–50 nm) high defect and grain boundary densities together with the transformation of β-Ta into α-Ta enable the diffusion of Cu at lower temperatures despite the presence of a thin oxide layer. It has been reported that Ta starts dissolving its native oxide layer in the same temperature region and at the time scale as that used in the present study.[34,35] To obtain more evidence for the essential role of the oxide formation and the subsequent dissolution, the hypothesis established in this study also needs to be investigated by utilizing the thermodynamically (critically) assessed Ta–O phase diagram and comparing the thermodynamic properties of the oxygen-containing solution phase and the Ta oxide. The results of the thermodynamic study will be published elsewhere.

The solubility of oxygen in 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 the segregation of oxygen in the grain boundaries of the Ta film inhibits Cu diffusion. Reduction of the grain boundary diffusion is achieved only with strongly segregating solutes,[36] i.e., with impurities having low solubility in the matrix phase. The improvement in the performance of Ta barrier layers with the help of small amounts of oxygen is in agreement with the results of Clevenger *et al.*[15] They observed the failure of an ultrahigh vacuum (UHV) Ta barrier layer to take place at a temperature as low as 320 °C, which was caused by the penetration of Cu through the Ta layer without formation of $TaSi_2$. Hence, a certain minimum level of oxygen is needed in the Ta barrier layer in order to have reasonable thermal stability. The required oxygen level may be incorporated into Ta film under normal HV conditions during the deposition.[15]

IV. CONCLUSIONS

Interfacial reactions in the Si/Ta/Cu metallization system were investigated. When the Ta layer was 100 nm thick, the first phase to form was $TaSi_2$. After $TaSi_2$ formation, the Cu atoms diffused through the layer mainly via the grain boundaries and reacted with silicon to form Cu_3Si. The latter reaction occurred abruptly at 685 °C, leading to complete failure of the metallization structure. However, when the Ta diffusion barrier layers were thin (10–50 nm), the diffusion of Cu into the Si substrate and the formation of Cu_3Si took place before the temperature of $TaSi_2$ formation (~650 °C). Nevertheless, the Cu overlayer enhanced the $TaSi_2$ formation and enabled its formation even at 600 °C after Cu penetration and nucleation of Cu_3Si. The formation of an amorphous layer at the Si/Ta interface was also observed with a transmission electron microscope. It imposes a lower limit on the thickness of the Ta barrier layer and may prevent its utilization with very small feature sizes. The role of oxygen is expected to be very important, because it has a strong effect on the stability of the barrier layer. It was suggested that a metastable TaO_x layer forms at the Ta/Cu interface and effectively prevents the diffusion of Cu into Ta by acting as an "additional" barrier layer. Only after this oxide layer has dissolved in the tantalum lattice can the diffusion of copper and the interfacial reactions proceed. The final reaction products, $TaSi_2$ and Cu_3Si, are in local equilibrium according to the calculated ternary phase diagram. Therefore, further reactions are not expected to take place in the Si/Ta/Cu system. This is in close agreement with the experimental results, which did not reveal any other phase in the samples.

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