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Copper Diffusion Into Silicon Substrates Through TaN and Ta/TaN Multilayer Barriers

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A study of copper (Cu) diffusion into silicon substrates through Ta nitride (TaN) and tantalum (Ta/TaN) layers was investigated based on an experimental approach. TaN_x and Ta/TaN_x thin films were deposited by radiofrequency sputtering under argon (Ar) and Ar-nitrogen (N) plasma. The influence of the N_2 partial pressure on the microstructure and the electrical properties is reported. X-ray diffraction patterns showed that the increase of the N_2 partial pressure, from 2 to 10.7%, induces a change in the composition of the δTaN phase, from TaN to $TaN_{1.13}$, as well as an evolution of the dominant crystallographic orientation. This composition change is related to a drastic increase of the electrical resistivity over a N_2 partial pressure of 7.3%. The efficiency of TaN layers and Ta/TaN multilayer diffusion barriers was investigated after annealing at temperatures between 600 and 900 °C in vacuum. Secondary ion mass spectrometry profiles showed that Cu diffuses from the surface layer through the TaN barrier from 600 °C. Cu diffusion mechanisms are modified in the presence of a Ta sublayer.

Keywords diffusion barrier, nitrides, reactive sputtering, thin films

1. Introduction

Advances in integrated circuit technology imply not only the development of new technologies for manufacturing but also new materials with improved performances. There has been a great interest recently in the use of copper (Cu) as on-chip metallization in microelectronic devices as well as in the development of an attractive class of refractory metal nitrides used as diffusion barriers. Cu has been chosen as a promising substitute for aluminum or aluminum-based alloys owing to its lower electrical resistivity and higher electromigration resistance.[1,2] However, Cu is well known for its easy diffusion and strong interaction with silicon (Si) or SiO_2, which results in degradation of the electrical integrity of the microelectronic devices by possible formation of Cu_3Si precipitates.[3] Moreover, Cu is a very undesirable dopant in Si semiconductors, generating a midgap defect level. Device failure occurs for Cu concentrations in the parts-per-million range, well before Cu silicides are formed. Thus, it is necessary to prevent the Cu diffusion under rapid thermal annealing by incorporating an efficient diffusion thin layer between Cu and Si or SiO_2 substrates.

Owing to both its low electrical resistivity, reducing the contact resistance, and excellent thermal stability, tantalum nitride (TaN) has received considerable interest as an efficient material for diffusion barriers.[4,5] It has a high melting point (3087 °C) and does not form intermetallic compounds with Cu, unlike tantalum (Ta). The TaN microstructures of thin films as well as electrical properties depend greatly on the deposition parameters.[6] Hence, in the reactive sputtering process chosen in this work, the N_2-to-argon (Ar) gas ratio was a major factor influencing the electrical resistivity of TaN thin films.[7]

Variations in stoichiometry are common in TaN films due to their defect structure.[8] Consequently, the properties of the films (e.g., microstructure and resistivity) strongly depend on the deposition conditions. The characteristics of TaN thin films are also very sensitive to deviation from stoichiometry,[9] and this material exists in many different stable or metastable phases.[10] Stacking one TaN thin film above a Ta thin film may improve the efficiency of the diffusion barrier according to the nature of the interfaces. There is a growing interest in graded Ta/TaN[11-13] or threefold graded Ta/TaN/Ta[14] barrier layer stacks.

In this article, the authors focused on the reliability of the TaN single layer and Ta/TaN multilayer systems vs. Cu diffusion. The aim of this work was, on the one hand, to relate the microstructural and electrical properties of TaN layers to the process route parameters and, on the other hand, to better understand the diffusion mechanisms of Cu to Si through TaN and Ta/TaN layers, the thickness of which varied from 80 to 180 nm. This work has to be considered as a first step in the understanding of the diffusion mechanisms in semiconductor devices, where the barriers are obviously thinner, typically near 10 nm. The originality of this work is in the diffusion mechanisms study,

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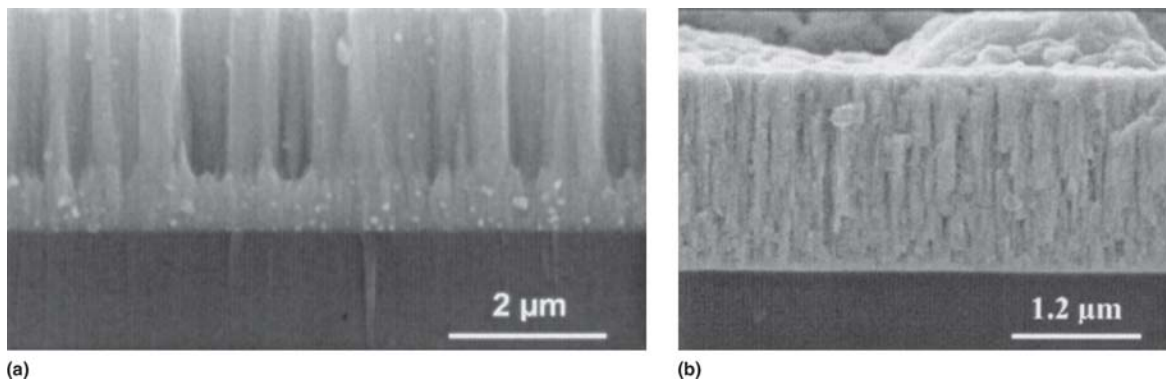

Fig. 1 SEM cross-sectional views of sputter-deposited layers (a) Ta and (b) TaN

which is based on an experimental approach, unusually coupling the double aspect (i.e., microstructure and diffusion).

2. Experimental

Ta and TaN thin films were deposited by radiofrequency (r.f.) sputtering under Ar or Ar-nitrogen (N_2) plasma using a Ta target (Johnson Matthey 2 in. diameter, 0.125 in. thick). Thin layers were sputter-deposited with a 90 W r.f. power either onto glass substrates, for the films characterization, or onto (100) Si wafers (2 in. diameter), for the diffusion study. The base pressure for each run was close to 1.10^{-4} Pa. The target-to-substrate distance was about 6 cm, the substrate holder being cooled or heated according to the expected characteristics of the thin films. Prior to the TaN thin film deposits, the target was cleaned by presputtering in Ar plasma with a shutter between the target and the substrate. At this stage, the presputtering was then continued in Ar-N plasma before TaN thin film deposition. Compared with other processes that allow the elaboration of thin layers, the r.f. sputtering offers better adherence of the deposited films as well as an easy and accurate monitoring of their thickness.

Freshly deposited TaN and Ta/TaN thin films are very sensitive to oxygen or moisture adsorption. All of the samples were placed in small polyethylene bags within an Ar-filled dry glove box where H_2O and O_2 contents were kept below 1 and 2 ppm, respectively.

A Dekta 3 profilometer (Veeco, Santa Barbara, CA) was used to rapidly measure the thickness of the layers. Scanning electron microscopy (SEM) (6300F; Jeol; Tokyo, Japan/S2600N; Hitachi, Tokyo, Japan) also allowed the thickness of thin films to be measured and the surface aspect to be observed. The resistivity of thin films was obtained from the sheet resistance measured by a 4-point probe system at room temperature. The variation in sheet resistance of as-deposited thin films as well as of annealed multilayer samples was determined with this method. The crystal structures of the thin layers were identified from x-ray diffraction (XRD) pattern using a θ-θ Seifert diffractometer (Rich Seifert Co., Ahrensburg, Germany) with a Cu target x-ray tube working at a 40 kV voltage and a 25 mA current.

To determine the reliability of the diffusion barriers, thin Cu films were sputter-deposited over the Ta/TaN thin layers. The Si/Ta/TaN/Cu multilayer samples were then annealed for 30 min at temperatures ranging from 600 to 900 °C in a vacuum (3.10^{-4} Pa). Elemental composition through the film thickness was obtained by means of secondary ion mass spectrometry (SIMS).

3. Results and Discussion

3.1 Ta and Ta Nitride Layers Microstructure

The Ta and TaN layers were found to show a columnar growth, whatever the chosen sputtering process conditions were (Fig. 1). This growth mechanism is similar to the model proposed by Movchan and Demchishin[15] and Thornton.[16,17] The zone model developed by Thornton[16,17] has been commonly applied to explain the microstructures in sputtered films.

Two distinct regions are observed, the first one composed of fine columns near to the substrate and the second one constituted of larger columns, as previously related by other authors.[18] In the initial stages of film formation, low-mobility adatoms are agglomerated and the clusters are nucleated on the substrate. Subsequently, the clusters grow in the three-dimensional mode (island growth), the grains coalesce, and the fine columnar region is formed. Small voids with high density may be formed at the grain boundaries of this zone near the substrate. This void formation mechanism was previously proposed by Lloyd et al.[19] and Nakahara[20] as the coalescence-induced void formation mechanism. The amorphous grains coalesce at the expense of small grains and grow in a direction perpendicular to the substrate, resulting in the columnar grain formation. Large voids at the grain boundaries will be formed during this columnar growth. As a consequence, the columnar grain structure with nanoscaled voids and density-deficient grain boundaries is most likely to be intrinsic in the deposited films.

The deposition rates of Ta and TaN layers were determined from the measurements of the layer thicknesses. This deposition rate of Ta thin films is close to 14 nm/min for the defined experimental conditions (i.e., a plasma power of 90 W and an Ar gas pressure of 6.5 Pa). For the TaN layers, the

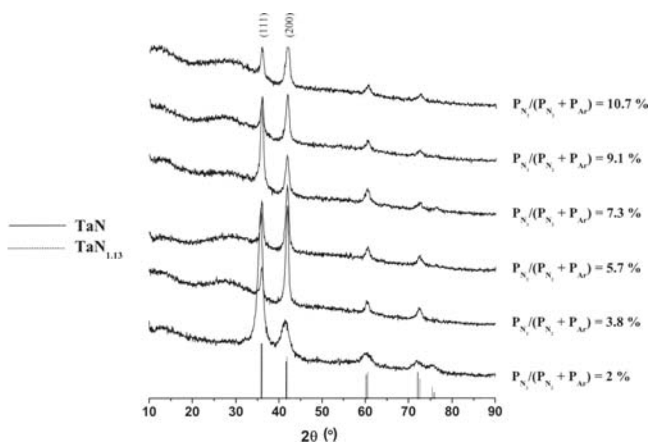

Fig. 2 XRD patterns of as-deposited TaN layers versus various N_2 gas partial pressures

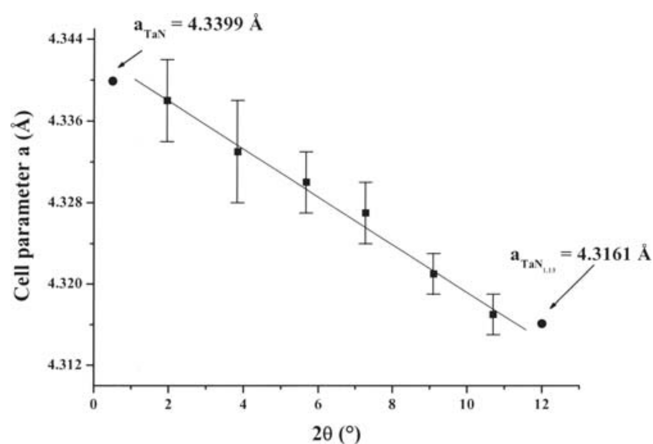

Fig. 3 N_2 partial pressure effect on the variation of the cell parameter

growth rate varies from 12 to 15 nm/min according to the sputtering process parameters; the details are reported in section 3.2.

3.2 Influence of the Nitrogen Partial Pressure on the Microstructure

As previously reported,[3,7] the properties of TaN films (i.e., microstructure and electrical properties) vary with the processing parameters (i.e., plasma power, partial N_2 gas pressure, and target-to-substrate distance). Because these parameters strongly depend on the deposition equipment, a part of this work was dedicated to the relation between the properties of the films and the processing parameters. In this section, the properties of TaN thin films are described according to the partial N_2 gas pressure.

TaN thin films were sputter-deposited under several partial N_2 gas pressures, with the Ar gas pressure of 6.5 Pa remaining constant. The plasma power and the sputtering time were 90 W and 2 h, respectively. The influence of the N_2 partial pressure on the microstructure was studied for a P_{N2}-to-(P_{Ar} + P_{N2}) ratio varying from 2.0 to 10.7%.

The partial N_2 gas pressure does not affect the growth mechanisms because a columnar growth is observed in every case. The deposition rate slightly decreases from 14.8 to 12.2 nm/min when the N gas pressure increases from 2.0 to 10.7%. This could be attributed to an overlapping layer that is grown on the cathode and leads to the poisoning of the target.[7] This poisoning effect decreases the number of open sites on the target surface for sputtering, as many sites on the target surface are occupied by N adatoms, or TaN_x-based compounds when the N_2 partial pressure increases.[21,22] However, this phenomenon is not relevant in the present experiments because only a slight decrease in the deposition rate was observed. Riekkinen et al.[7] related that the deposition rate decreased almost linearly with an increase of N_2 partial pressure and that increasing the N flow from 5 to 10% cuts the deposition rate to one third (0.7–0.5 nm/s). Nie et al.[23] showed that the deposition rate decreases almost linearly from 11.7 to 6.7 nm/min with the

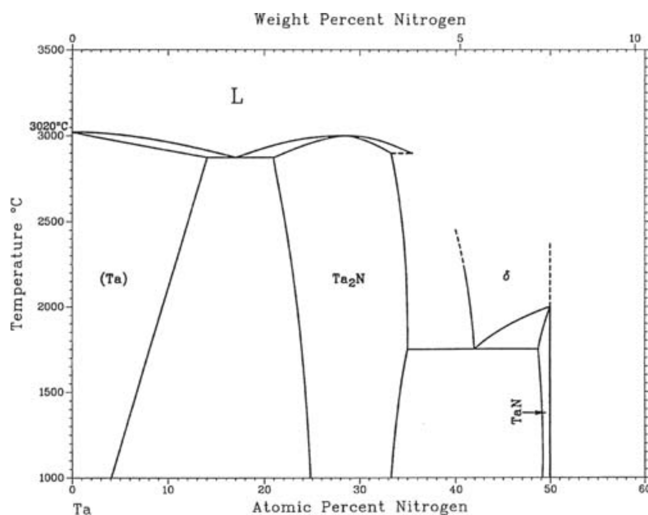

Fig. 4 Ta-N binary phase diagram[26]

increase of the N_2 partial pressure from 0 to 30%. However, the linear dependence of growth rate on N_2 partial pressure, which was observed by Nie et al.,[23] is also associated with phase changes in the films. These results show that, even under the same N_2 partial pressure, the growth mechanism of the TaN films greatly depends on the deposition system and processing parameters.

The XRD patterns showed that thin TaN films, δTaN, are formed with a NaCl-type structure, whatever the N_2 partial pressure is (Fig. 2). The increase of the N_2 partial pressure induces a change in the composition of the TaN phase, from stoichiometric TaN to overstoichiometric $TaN_{1.13}$. This results in a continuous change in cell parameter with composition from 4.3373 to 4.3160 Å, values that are close to the theoretical ones of 4.3399 and 4.3161 Å (Fig. 3). This composition change is associated with an evolution of the dominant crystallographic orientation. A variation of the I(111)-to-I(200) intensity ratio with the N_2 partial pressure was observed. The (200) orientation becomes dominant at the expense of the (111) orientation as the N_2 partial pressure is

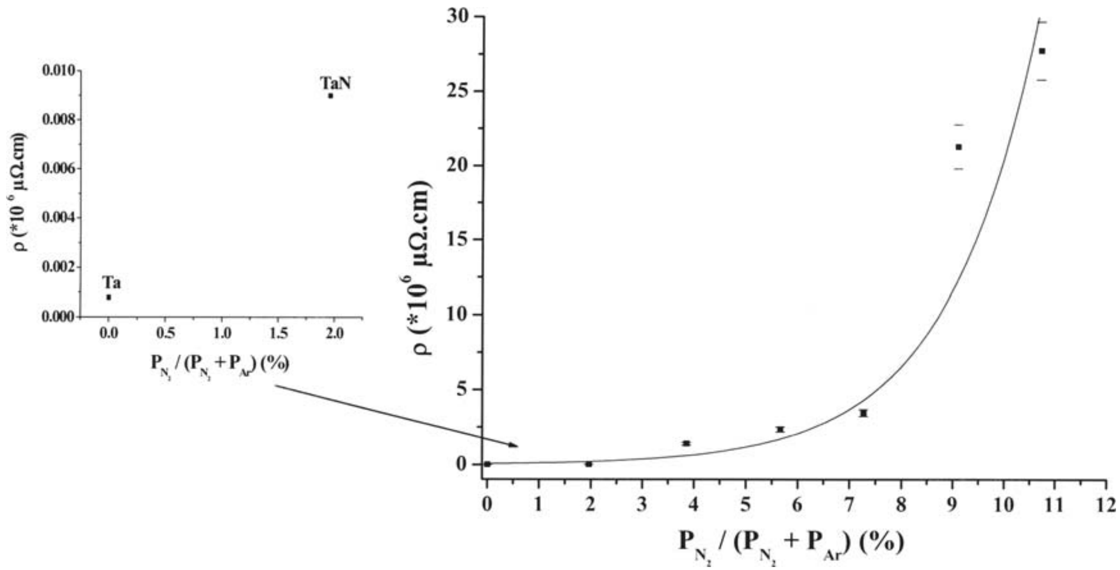

Fig. 5 N_2 partial pressure effect on the electrical resistivity of TaN films

Fig. 6 SIMS profiles performed on Cu/TaN/Si multilayer (a) as-deposited and after 30 min of vacuum annealing at (b) 600 °C, (c) 800 °C, and (d) 900 °C

increased from 2 to 3.8%. The (111) intensity is similar to the (200) intensity for a N_2 partial pressure of 5.7% and gets larger for N_2 partial pressures from 7.3% up to 10.7%. Tsukimoto et al.[18] also observed that the I(111)-to-I(200) intensity ratio decreased when the N_2 partial flow increased from 5 to 10%, which indicates that the (111) fiber structure became weaker with increasing N_2 flow rates. For higher N_2 partial pressure, Nie et al.[23] found evidence for a variation of the dominant orientation. The (111) orientation became dominant at the expense of the (200) orientation as the N_2 partial pressure was increased from 15 to 20% up to 30% in the sputtering gas. Thus, the phase formation sequences as a function of the N_2 flow are not always comparable between different studies. However, it is shown that the composition of TaN_x films is affected by the N_2 flow ratio during reactive sputtering.[24,25]

The present experiments show that TaN films are very sensitive to deviation from stoichiometry according to the process parameters. This may be explained considering the Ta-N binary phase diagram[26] (Fig. 4). In this phase diagram, the Ta_2N phase is stable in a relatively large N concentration range (~25–33 at.%), and the process window is therefore wide. Additional N in the film will cause a mixture of the Ta_2N and δTaN phases to form. The δTaN phase is located in a very small region in the phase diagram (~49–50 at.%), causing the process window to be narrow.

The XRD patterns indicate the presence of an amorphous phase. One can expect some amount of amorphous TaN material in the film, where crystalline grains are embedded.[24] It is worth being noted that the cubic δTaN phase can be easily formed in the as-deposited film when a suitable N_2 partial pressure is applied. In a bulk TaN system prepared by heating Ta in high-pressure N_2, metastable cubic δTaN can only be obtained at very high temperatures (e.g., 1700 °C).[27] This implies that, in a sputtering process, the energy needed for forming the cubic TaN phase could be obtained from the high energetic ions in the plasma generated by the r.f. or direct current power.[28]

The resistivity of the as-deposited films as a function of the N_2 partial pressure is shown in Fig. 5. An increase of the electrical resistivity from 9.10^3 to $3.5.10^6$ μΩ/cm is observed when the partial N_2 pressure increases from 2-7.3%. A further addition of N_2 (>7.3%) causes a drastic increase in resistivity. This evolution is related to the change in N composition previously observed, from stoichiometric TaN to overstoichiometric $TaN_{1.13}$. These results are in good agreement with data from the literature.[7,23,29,30] The steeply increased resistivity is attributed to the formation of the N-rich phase when increasing the N_2 partial pressure. Other N-rich compounds, like Ta_5N_6, Ta_4N_5, and Ta_3N_5, have also been reported.[31] No signs of such phases in the XRD patterns were observed in the present work, which may be attributed to the relatively low N_2 partial pressure.

3.3 Diffusion Study

The efficiency of TaN and Ta/TaN diffusion barriers was studied from profiles obtained by SIMS, which was performed on samples annealed for 30 min at 600, 800, and 900 °C in a vacuum. The thicknesses of the different layers were calculated from the SIMS abrasion rate and were 96 nm for the TaN single layer and 130 nm/180 nm for the Ta/TaN multilayer.

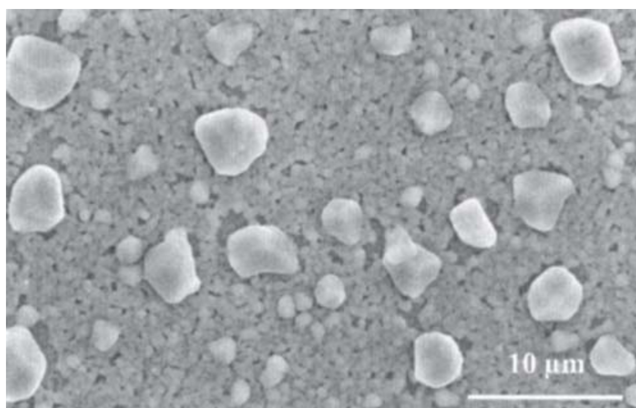

Fig. 7 Cu silicide precipitates observed after vacuum annealing at 800 °C for 30 min

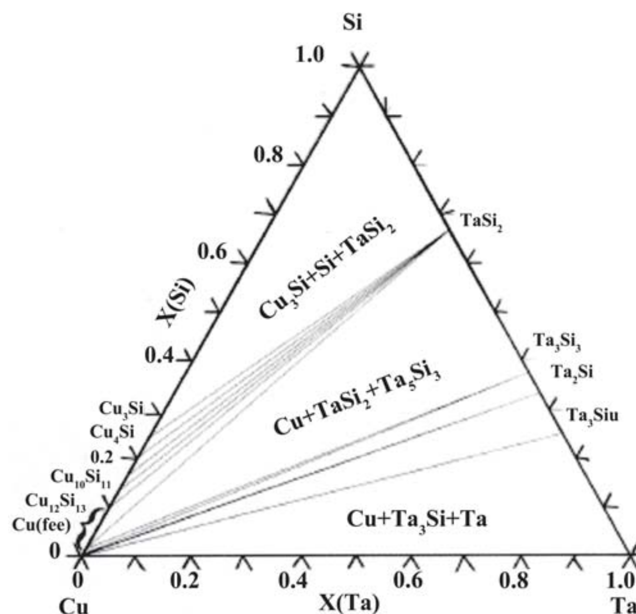

Fig. 8 Isothermal section of the Si-Ta-Cu phase diagram at 700 °C[33]

3.3.1 Diffusion Study of Cu Through a TaN Barrier. After annealing at 600 °C, Cu diffuses linearly through the TaN barrier thickness, as shown in Fig. 6 where SIMS profiles are reported for as-deposited and annealed samples. An increase of the annealing temperature to 800 °C induces the total diffusion of Cu to the Si substrate through the TaN barrier. The simultaneous diffusion of Ta and N through the Cu surface is also observed. These diffusion phenomena are enhanced after annealing at 900 °C.

The SEM observations showed that precipitates are formed at the surface of the sample after annealing at 800 and 900 °C (Fig. 7). These are thought to be Cu_3Si precipitates, which are formed at the Si-TaN interface due to the

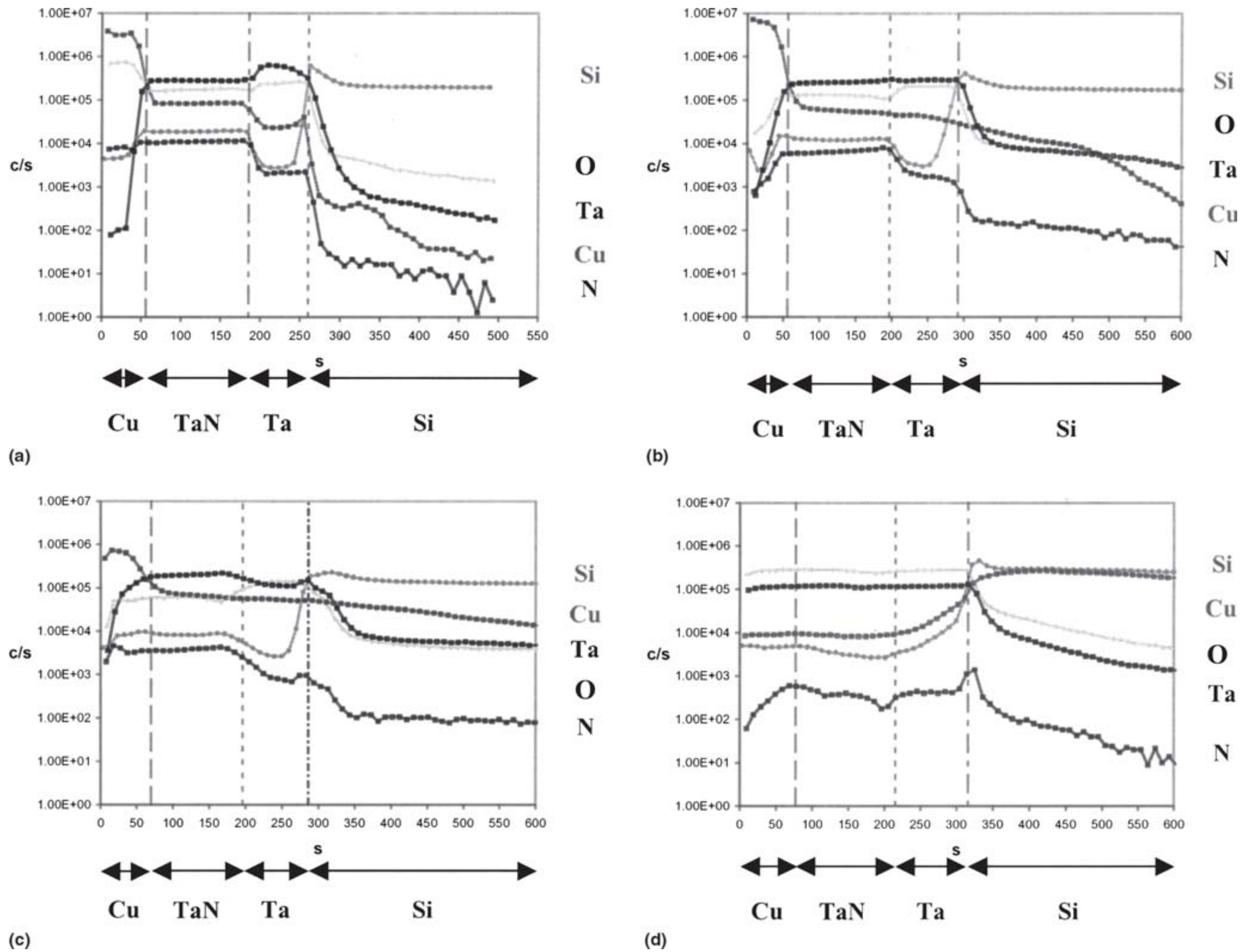

Fig. 9 SIMS profiles performed on Si/Ta/TaN/Cu multilayer (a) as-deposited and after 30 min of vacuum annealing at (b) 600 °C, (c) 800 °C, and (d) 900 °C

diffusion of Cu through the TaN layer. The nucleation of Cu_3Si in Si is associated with a large volumic expansion of 150%, leading into stress relaxation and the production of intrinsic point defects.[32,33] As previously described, the TaN layer showed a columnar growth. So, the diffusion mechanism may be assumed to be the Cu diffusion to the Si-TaN interface through the TaN intercolumns voids, which may be considered as the major diffusion paths. Ta silicide compounds are also observed to be formed. Similar results were obtained by Yang et al.,[29] who studied the efficiency of a 50 nm thick TaN diffusion barrier after 30 min of vacuum annealing. The authors showed that a small number of Cu atoms diffused into the Si substrate after 500 °C annealing, which does not affect the Cu sheet resistance significantly. However, they observed a large amount of interdiffusion between Cu and Si after 700 °C annealing, resulting in a drastic increase of Cu sheet resistance. Simultaneous diffusion of Ta to the surface was also observed. The high-temperature failure of barrier capability for the TaN films was then attributed to the interdiffusion of Cu and Si, forming Cu_3Si-related precipitates. Yang et al.[29] assumed that interdiffusion may be enhanced by the microstructure and resulting roughness of the TaN surface.

A ternary Si-Ta-Cu phase diagram was calculated from the assessed binary thermodynamic data by Laurila et al.[33] and is shown at 700 °C in Fig. 8. The presence of $TaSi_2$ is predicted from the phase diagram, because it is in local equilibrium both with Cu_3Si and Si. However, the Ta/Si reactivity decreases in the presence of N.[34]

From these experimental results, it may be supposed that microstructure is important to the stability of TaN thin film as a diffusion barrier. To experimentally demonstrate this requires the observation of two different microstructures having different stability. That is the reason why Ta/TaN bilayer barriers were sputter-deposited to obtain a noncontinuous columnar growth. This should result in better efficiency of the diffusion barrier due to the nonstraight diffusion paths obtained.

3.3.2 Diffusion Study of Cu Through Ta/TaN Multilayer Barrier. The role of a Ta sublayer on the Cu diffusion to the Si substrate was studied while preparing Si/Ta/TaN/Cu multilayer samples. The SIMS profiles showed that

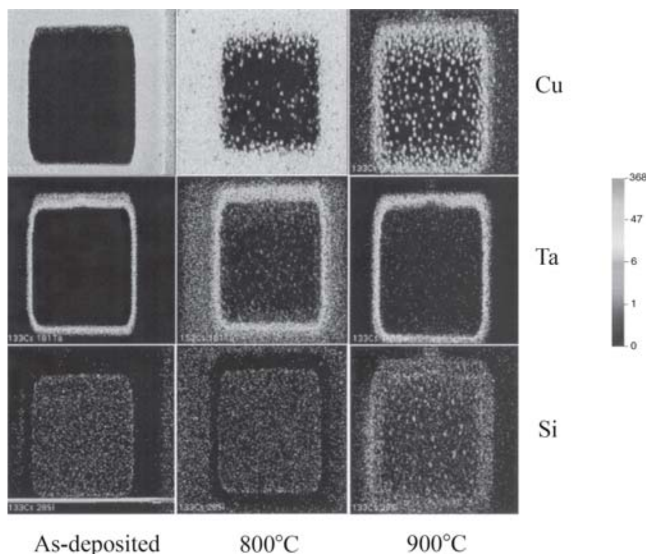

Fig. 10 Elemental SIMS images of Si/Ta/TaN/Cu as-deposited and after 30 min annealing at 800 and 900 °C

mechanisms of Cu diffusion are modified in the presence of a Ta sublayer after annealing at 600 °C, if compared with the single TaN barrier (Fig. 9). The Ta sublayer may be supposed to reduce the diffusion because a significant amount of Cu remains at the sample surface, which may be attributed to the noncontinuous columnar structure of the Ta/TaN bilayer . However, it is difficult to discuss Cu diffusion into the Si substrate because the matrix effects occurring during SIMS analyses may affect the signal. Further investigations will be necessary to determine the role of the Ta sublayer on Cu diffusion into a Si substrate.

After annealing at 800 °C, Cu diffusion seems to be reduced in the presence of a Ta sublayer because some Cu still remains at the sample surface and no diffusion of Ta to the surface is observed. After annealing at 900 °C, the Ta sublayer does not have any effect on the diffusion mechanisms because the diffusion of Cu to the Si substrate and Ta to the surface is observed.

Elemental images were recorded from SIMS analyses performed on Cu/Ta/TaN/Si multilayer samples after annealing at 800 and 900 °C. The thicknesses of the Ta and TaN layers were 77 and 93 nm, respectively. These images show the elemental distribution through the thickness of the abrasion crater performed during SIMS analyses (Fig. 10). The Cu diffusion to the Si substrate was observed as well as the formation of Cu-rich precipitates, after annealing at 800 and 900 °C. These images illustrate the role of the barrier thickness because Ta diffusion to the surface is now observed after annealing at 800 °C and is a consequence of the lower barrier thickness.

4. Conclusions

The diffusion of Cu to Si substrates through TaN and Ta/TaN thin layers was studied. Thin films were r.f. sputter-deposited under Ar or Ar/N_2 plasma for Ta and TaN layers, respectively. The properties of TaN_x layers were observed to be affected by the plasma N_2 partial pressure. A drastic increase in resistivity is measured when the N_2 content is >7.3%, and is related to a composition change of the TaN phase from stoichiometric TaN to overstoichiometric $TaN_{1.13}$. The efficiency of TaN and Ta/TaN diffusion barriers was studied after 30 min of annealing at temperatures from 600 to 900 °C in a vacuum. Regarding the TaN barrier, it appears that Cu diffuses through the TaN layer at and above 600 °C. The columnar microstructure of the layers was supposed to be important to the stability of TaN thin film as a diffusion barrier. A change in the Cu diffusion mechanism was observed in the presence of a Ta sublayer at 600 °C. Further investigation will be necessary for a better understanding of the role of the Ta sublayer on the diffusion mechanisms.

In the future, the potential of new materials for use as diffusion barriers may be determined from phase diagram calculations (Thermocalc). Even though the complete thermodynamic equilibria are never met in thin film systems—because the materials at the contact regions are under continuous microstructural evolution—the local equilibrium is, however, generally attained at the interfaces. Therefore, the phase diagrams provide an efficient method for designing the diffusion barrier layer between various metallizations, especially when they can be combined with kinetic information.

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