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Thermal oxidation of amorphous ternary $Ta_{36}Si_{14}N_{50}$ thin films

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(Received 25 March 1991; accepted for publication 6 June 1991)

The oxidation kinetics of reactively sputtered amorphous $Ta_{36}Si_{14}N_{50}$ thin films are studied in dry and wet ambient in the temperature range of 650–850 °C by backscattering spectrometry, Dektak profilometer, and x-ray diffraction analyses. The dry oxidation is well described by a parabolic time dependence which corresponds to a process controlled by the diffusion of the oxidant in the oxide. The growth of the oxide in wet ambient is initially very rapid and then proceeds linearly which means that the process is reaction limited. Both oxidation rates are thermally activated. The activation energies are 2.0 eV for dry and 1.4 eV for wet ambient. The pre-exponential factors are 0.17×10^{16} Å^2/min and 7.4×10^{8} Å/min, respectively. Both the dry and wet oxidation of the amorphous ternary $Ta_{36}Si_{14}N_{50}$ film result in the formation of an x-ray amorphous $Ta_{14}Si_{5.5}O_{80}$ layer.

I. INTRODUCTION

The advances in silicon technology impose severe requirements on the stability of metal-semiconductor contacts. Therefore, diffusion barriers in the form of an electrically conducting thin film are used to minimize deleterious interactions between a conducting layer and the semiconductor.[1] In VLSI (very large-scale integration) devices, it is favorable to retain the stability of the barrier during an oxidation process. On the other hand, some special applications may require an option to grow a thermal oxide for isolation of the metallization and final passivation of devices. The oxidation behavior of diffusion barriers is, hence, relevant in assessing their possible applications. Oxidation is also interesting from the point of view of material properties.

Amorphous Ta-Si-N alloys offer a barrier performance between ⟨Si⟩ and Al or Cu overlayers that surpasses that of all commonly known thin-film barriers.[2–4] The effectiveness of amorphous Ta-Si-N alloy barriers has also been tested for Au on silicon.[5] The behavior of Ta-Si-N alloy films under exposure to oxidizing ambients is therefore of significance. The crystallization temperature of this ternary alloy is around 1100 °C.[2]

Generally, transition metal nitrides transform to oxides at elevated temperatures in an oxidizing atmosphere. A comparison between the heats of formation of oxides, nitrides, and silicides of Ta, and oxides and nitrides of Si (Table I) suggests that Ta-Si-N should transform to a mixture of Ta_2O_5 and SiO_2 during a thermal oxidation. It is also known that refractory metal oxides tend towards a nonstoichiometric structure due to the oxygen deficiency. The oxidation of a number of transition metal nitrides, like tantalum nitride,[9] titanium nitride,[10,11] hafnium nitride,[11] and tungsten nitride[12] has been studied. The results have usually been interpreted in terms of the oxidant diffusing through the growing oxide and limiting the oxidation rate, which means that the oxidation process follows the parabolic growth law.

In this study, we report on the oxidation behavior of reactively radio-frequency (rf) sputtered amorphous $Ta_{36}Si_{14}N_{50}$ films for dry and wet oxidation in the temperature range of 650–850 °C.

II. EXPERIMENTAL PROCEDURES

Chemically cleaned ⟨100⟩-oriented *n*-type silicon substrates, with or without thermally grown SiO_2 layers about 700-nm thick, and carbon substrates were loaded into a sputtering chamber which was then pumped down to a base pressure of about 5×10^{-7} Torr. Tantalum-silicon-nitride films were rf sputtered in an Ar-N_2 plasma from a Ta_5Si_3 target with a forward sputtering power of 300 W without dc bias on the substrates. The total gas pressure was 10 mTorr and the relative nitrogen partial pressure was 5%. The argon to nitrogen flow ratios as well as the total gas pressure were adjusted by flow controllers and monitored with a capacitive manometer in a feedback loop.

Two separate depositions were performed. First, a Ta-Si-N film only about 100-nm-thick film was sputter-deposited on carbon, oxidized silicon, and bare ⟨Si⟩ substrates. These thin Ta-Si-N samples were used to derive the composition of the film by comparing the backscattering signal heights of each element, and to study the changes in atomic profiles in detail during the oxidation process.

In the second deposition, a Ta-Si-N film about 500-nm-thick was sputtered on patterned silicon and ⟨Si⟩/SiO_2 substrates to determine the atomic densities of the film before and after oxidations, and for studies of the oxidation kinetics, respectively. The atomic density of Ta-Si-N was calculated from the thickness of the film measured by a Dektak profilometer and from the energy width of the backscattering signal of Ta. The stopping cross sections for Ta and Si were taken from Ref. 13 and that for N from Ref. 14.

The sputtered amorphous ternary films were oxidized in an open-ended quartz tube furnace. The oxygen gas flow was adjusted to 100 cm^3/min and fed into the furnace tube either directly (*dry oxidation*) or by bubbling it through a bottle of hot (96 °C) deionized water prior to entering the furnace (*wet oxidation*).

Thin (100-nm) Ta-Si-N films on both oxidized silicon

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TABLE I. Heat of formations for Ta-O, Ta-N, Si-O, Si-N, and Ta-Si compounds. All the data is according to Goldschmidt[a] unless otherwise stated.

Compound	Heat of formation (kcal/g mol)
TaN	-59
Ta_2N	-64
Ta_2O_5	-499
SiO_2	-205[a]
Si_3N_4	-179[b]
$TaSi_2$	-24[c]
Ta_2Si	-30
Ta_5Si_3	-72[c]
$Ta_{4.5}Si$	-32

[a]See Ref. 6.
[b]Data from Ref. 7.
[c]Data from Ref. 8.

and bare silicon wafers were oxidized completely in dry oxygen at 750 °C for 40 min. The structure and the composition of the films were studied via Read camera x-ray diffractrometry and backscattering spectrometry before and after the oxidation. The composition was calculated comparing the signal heights of each element and using the stopping cross sections for Ta and Si from Ref. 13, and that for N and O from Ref. 14. The determination was based on methods given in Ref. 13.

The thick Ta-Si-N film on a patterned silicon substrate was completely oxidized in dry ambient at 850 °C for 5 h. The backscattering spectrum confirmed that the Ta-Si-N is fully transformed to Ta-Si-O. The Dektak profilometer was used to measure the thickness of oxidized film. The determination of the atomic density was carried out using backscattering spectrometry in conjunction with Dektak profilometer measurements.

The oxidation temperatures for various times for the thick (500-nm) Ta-Si-N films on ⟨Si⟩/SiO_2 substrates were 650, 700, 750, 800, and 850 °C. The thicknesses of the oxide layers on Ta-Si-N thin films were then derived directly from 2 MeV $^4He^{++}$ backscattering spectra by comparing their backscattering spectra against that of the calibrated reference sample.

III. RESULTS

A. Characterization of the oxidized thin Ta-Si-N layer

The backscattering spectrum of an as-deposited Ta-Si-N film sputtered on a ⟨Si⟩ substrate reveals the main elements Ta, Si, and N in the layer and some amount of Ar impurity (Fig. 1). The composition of the as-deposited Ta-Si-N is approximately $Ta_{36}Si_{14}N_{50}$ with an estimate error of $\pm 5\%$. The Ar content in the film is about 3.3 at. %. Both determinations agree well with the results of Kolawa *et al.*[2] The density is 8.4×10^{22} atoms/cm^3, the microstructure is x-ray amorphous, and the thickness of the ternary thin film is 90 nm determined by backscattering spectrometry.

A drastic change in the backscattering spectrum is observed after complete oxidation of the film at 750 °C for 40

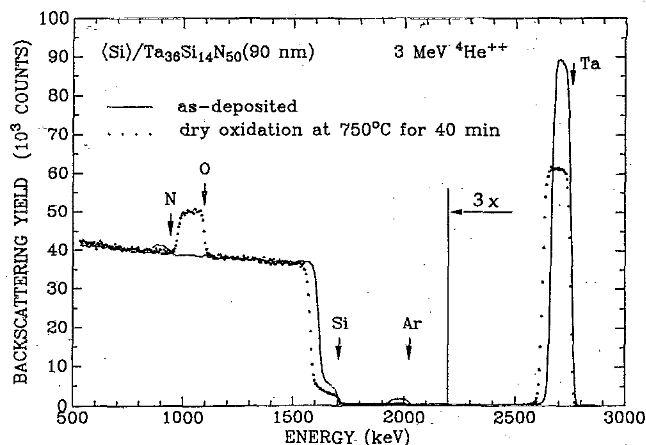

FIG. 1. 3 MeV $^4He^{++}$ backscattering spectra obtained with normal incidence of the beam on a ⟨Si⟩/$Ta_{36}Si_{14}N_{50}$ (90 nm) sample before and after oxidation in dry ambient at 750 °C for 40 min. The scattering angle of detected particles is 170°.

min (Fig. 1): the Ta-Si-N alloy is transformed into a mixture of Ta, Si, and O. The nitrogen and argon signals are absent, revealing a release of both of these two elements from the film. Interestingly, silicon is still uniformly distributed over the cross section of the layer. Also, the signals of all these elements are well defined. Visually, the sample surface is smooth and uniform. The composition of the film obtained by comparing the signal heights of each element after the oxidation gives a Ta:Si:O ratio which is approximately 14:5.5:80 with an error of about $\pm 5\%$. This completely oxidized film is x-ray amorphous.

B. Oxidation kinetics of the thick Ta-Si-N

A complete oxidation of the 500-nm-thick Ta-Si-N alloy film yields an approximately 1200-nm-thick oxide layer, both thicknesses as determined by a profilometer. In addition, assuming that the composition of the oxidized $Ta_{36}Si_{14}N_{50}$ film is $Ta_{14}Si_{5.5}O_{80}$ as determined on the thin film we derive a density of about 6.6×10^{22} atoms/cm^3 for the oxide layer. This atom density has been used to derive the thickness of the oxide layers from backscattering spectra in a manner described in Ref. 13.

After isothermal oxidations at 650, 700, 750, 800, and 850 °C for various times in both dry and wet ambients, backscattering analyses reveal a gradual increase of the oxide thickness with oxidation time, plotted in Fig. 2. A sharp oxide-nitride interface exists in the backscattering spectra of partially oxidized Ta-Si-N layer (Fig. 3). The well-defined signals in the backscattering spectrum indicate also that the composition of the oxide layer is relatively uniform in depth. The composition of the oxide layer was determined to be around $Ta_{14}Si_{5.5}O_{80}$ in all samples within the error of 5%. For all temperature-time variations, the wet oxidation is faster than that of the dry oxidation. The oxide growths at 800 °C in both dry and wet ambient are plotted in Figs. 4(a) and 4(b).

Dry oxidation: In Fig. 4(a), the oxide thickness is plotted in open circles (left scale) while the oxide thickness

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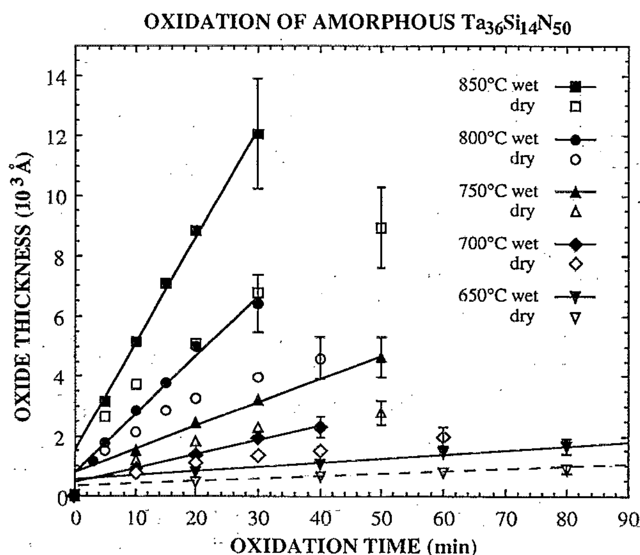


FIG. 2. The oxide thickness vs the oxidation time at various temperatures. The open characters are the data points of the dry oxidation and the filled ones are those of the wet oxidation. Where a linear time dependence holds, a straight line (a dotted straight line for 650 °C dry) from a regression analysis has been drawn in the figure.

squared is plotted in open rectangles (right scale) as a function of the oxidation time. The oxidation is clearly parabolic, not linear, and a good fit of the data points is obtained. The rate constant corresponding to the slope of the straight line in Fig. 4(a) is then $B(800\,°C) = 0.53 \times 10^6$ Å^2/min. In the temperature range of 700–850 °C, the oxide is observed to grow parabolically according to the relationship

$$d^2 = Bt, \tag{1}$$

where d is the oxide thickness, B the parabolic rate constant, and t the oxidation time. At 650 °C the growth law

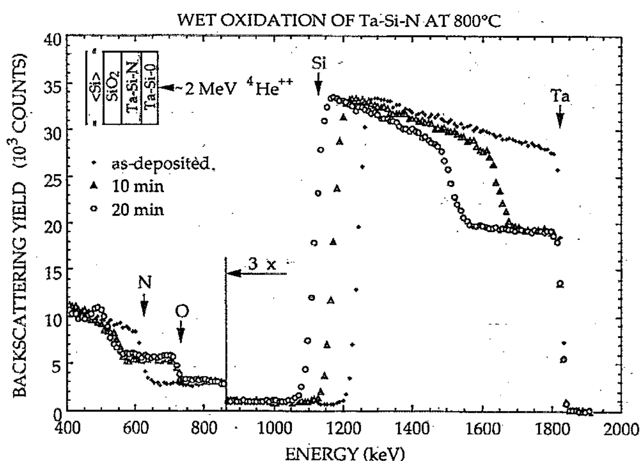
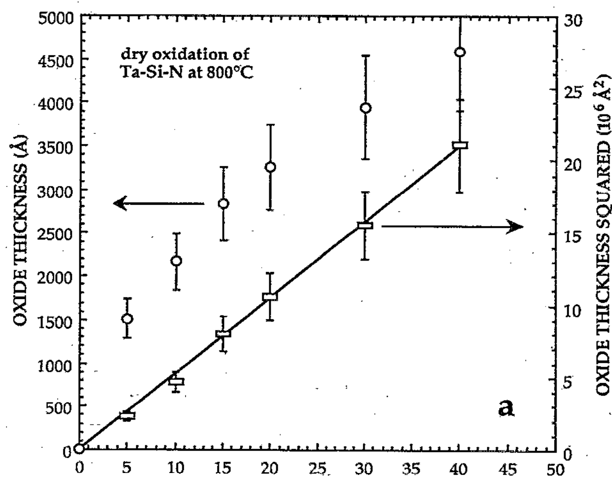


FIG. 3. 2 MeV $^4He^{++}$ backscattering spectra of a series of identical $\langle Si \rangle / SiO_2 / Ta_{36}Si_{14}N_{50}$ structures before and after oxidations in wet ambient at 800 °C for various times. The scattering angle of detected particles is 170 °C, and the angle between the incident beam and the sample normal is 6°.



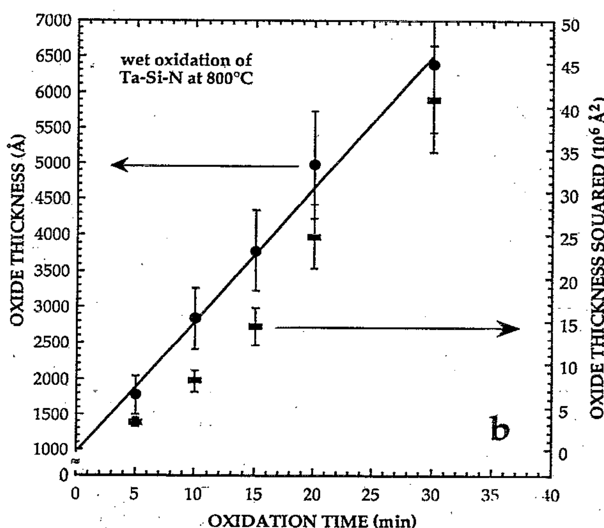


FIG. 4. (a) The thickness (open circles) and the thickness squared (open rectangles) of the oxide layer of a Ta-Si-N film plotted as a function of the oxidation time at 800 °C for a dry oxidation. (b) The thickness (filled circles) and the thickness squared (filled rectangles) of the oxide layer on Ta-Si-N plotted as a function of the oxidation time for wet oxidation at 800 °C.

shifts to a time dependence that is more roughly linear than parabolic which suggests a change in the rate-limiting mechanism of oxidation. The oxidation at this point is rather described by a linear time dependence. In addition, the regression analysis of the data reveals an initial rapid oxide phase formation in the film at 650 °C.

The rate constants are presented on a logarithmic scale as a function of the temperature in degrees centigrade (upper scale) and in reciprocal temperature (lower scale) in Fig. 5 (dry). The linear fit of the data corresponds to the exponential Arrhenius relationship of the form

$$B = B_0 \exp(-E_a/kT), \tag{2}$$

where B is the parabolic time-dependence, B_0 the temperature independent pre-exponential factor, E_a the thermal activation energy associated with the oxidation process, k is the Boltzmann coefficient, and T the oxidation temperature in degrees Kelvin. Fitting Eq. (2) to the regression

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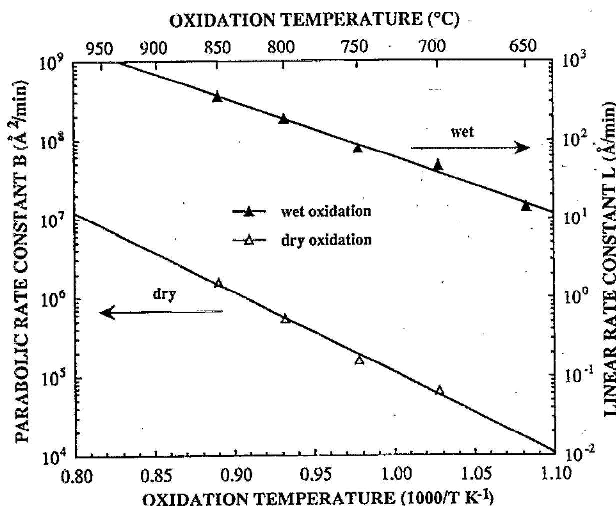

FIG. 5. The parabolic rate constant $B(d^2 = Bt)$ for the dry oxidation and the linear rate constant $L[d = L(t + \tau)]$ for the wet oxidation of rf-sputtered amorphous $Ta_{36}Si_{14}N_{50}$ film vs reciprocal oxidation temperature.

line gives $B = 0.17 \times 10^{16}$ Å²/min and $E_a = 2.0$ eV (expected error for both values 5%) for dry oxidation between 700–850 °C.

Wet oxidation: As shown in Fig. 4(b), the oxide grows linearly (filled circles), not parabolically (filled rectangles) at 800 °C. The oxidation proceeds similarly throughout the experimental temperature region. The data can be fitted to a straight line

$$d = L(t + \tau), \tag{3}$$

where L is the linear rate constant and τ a fitting parameter which accounts for the initial rapid growth of an oxide phase. A distinct rapid initial oxide growth is observed which is also a function of the temperature (Fig. 2). The rate constant corresponding to the slope of the linear plot in Fig. 4(b) is $L(800\,°C) = 187$ Å/min.

Presenting the slopes as a function of the reciprocal temperature (Fig. 5: wet) the data can be fitted by an equation

$$L = L_0 \exp(-E_a/kT), \tag{4}$$

where L_0 is the linear rate constant. Values of $L_0 = 7.4 \times 10^8$ Å/min and $E_a = 1.4$ eV are derived from an exponential regression analysis of the data. The expected error for both determinations is approximately 5%.

IV. DISCUSSION

A. Structure and composition of oxide

As stated in the introduction section, the rf sputtered ternary Ta-Si-N alloy is expected to transform to a mixture of Ta_2O_5 and SiO_2 during an oxidation process. We do, in fact, observe that both Ta and Si are oxidized. The resulting oxide layer is generally amorphous. Even after the dry oxidation at 850 °C for 50 min, the highest temperature and time applied for the thick (500 nm) Ta-Si-N sample, diffuse rings associated with an amorphous structure are still present in the diffraction pattern together with some sharp Ta_2O_5 rings. An amorphous Ta_2O_5 phase has been found when a sputtered Ta_2N film was oxidized above 550 °C.[15]

It is well established that only the growth of SiO_2 takes place during the oxidation process around 1000 °C when $TaSi_2$ is deposited on Si.[16] In the same study, both SiO_2 and Ta_2O_5 are observed when $TaSi_2$ was deposited on oxidized silicon wafers. This dissimilarity in compound formation can easily be explained with the ternary phase diagram,[17] the difference being that in one case, the substrate is part of the system, but not in the other. In the present study, the Ta-SI-N film is sputter deposited on both silicon and oxidized silicon. We observe, however, that the dry oxidation of the thin Ta-Si-N film results in the same $Ta_{14}Si_{5.5}O_{80}$ composition of the oxidized film on both ⟨Si⟩ or ⟨Si⟩/SiO_2 substrates. A selective silicon dioxide formation on the surface of Ta-Si-N on silicon does not occur because a reaction of Ta and N with the Si substrate is kinetically inhibited. Diffusion of Ta and Si in the ternary alloy is evidently negligible. That finding is consistent with the crystallization temperature of $Ta_{36}Si_{14}N_{50}$ of about 1100 °C.[2] The oxidation of an amorphous Ta-Si-N thin film therefore leads to a formation of oxides of Ta and Si (Table I). However, the composition we find in the oxidized film does not agree with a mixture of Ta_2O_5 and SiO_2 phases. There is an excess of oxygen of about 34 at. % in the film.

B. Oxidation kinetics and mechanisms

Both Ta metal and silicon in the ternary Ta-Si-N film do readily oxidize in our study. The oxidation of the film is, in fact, a combination of these two processes.

Dry oxidation: A diffusion-limited mechanism governs the dry oxidation of Ta-Si-N in the temperature range of 700–850 °C. The oxidation process is thermally activated and the activation energy is 2.0 eV.

Steidel *et al.* found that the dry oxidation of bcc Ta, β-Ta, and Ta_2N films (on barium alumina borosilicate glass or on sapphire substrates) also follows a parabolic time dependence between 100–525 °C.[15] A dry oxidation at 525 °C for 1 h results in a formation of an approximately 3400-Å-thick oxide film on both bcc Ta and β-Ta. The activation energy 1.4 eV is close to the value (1.45 eV) given by Brady *et al.* for dry oxidation of Ta-N at 250–350 °C.[9] The resulting Ta_2O_5 oxide in the former study was amorphous.

It should be noted here that for transition-metal silicides on silicon in general, the oxidation mechanism and also the activation energy resemble those of single-crystal silicon because in both cases, SiO_2 forms.[17,18] Also, the oxidation of silicides is significantly slower than that of any thin-film alloys discussed here. The activation energy is 1.2 eV for dry oxidation of single-crystal silicon.[18] The results by the same authors reveal that less than 100-Å-thick oxide layer forms after oxidizing silicon at 800 °C for 1 h in dry oxygen.[18]

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An oxidation process, similar to the observations with Ta metal, its nitrides, and single-crystal silicon applies presumably in our study, too. The activation energies vary, however, partly due to different experimental methods and partly due to dissimilar thermodynamic stabilities of the film materials. The oxidation rate of the ternary Ta-Si-N alloy film is evidently slower than that of Ta metals or Ta-N films. On the other hand, the oxidation of single-crystal silicon proceeds much slower than that of ternary Ta-Si-N (one hour oxidation at 800 °C yields an about 5000-Å-thick oxide film, Fig. 4).

The different oxidation rate law that we observe at 650 °C in dry ambient for the ternary Ta-Si-N film, must indicate that the oxidation mechanism and kinetics apparently shift with temperature. Since our experiments were carried out in the region 650–850 °C, we cannot fully conclude the reasons for that phenomenon. Low-temperature-induced shifts in oxidation mechanism has been reported for Ta-N films.[9]

The oxidation kinetics of the $W_{80}N_{20}$ films which are also amorphous, has been studied.[12] The oxidation proceeds parabolically in time and the activation energy determined between 500–575 °C is 2.5 eV for dry oxygen. A change in the oxidation mechanism is recorded at 450 °C, too.

Wet oxidation: The activation energy for the linear oxide growth on the ternary Ta-Si-N film is 1.4 eV in the temperature range of 650–850 °C. The offset at $t=0$ of the straight line fitted to the data points at $t=0$ (Fig. 2) reveals that the wet oxidation is very rapid during the first few minutes, resulting in a 50–150-nm-thick oxide layer, depending on the oxidation temperature. As the oxidation process continues, the oxide growth rate decreases significantly and starts to follow a linear time dependence. A similar rapid initial oxidation phase is consistently found in all experiments where silicon is oxidized in dry oxygen.[19]

A study by Kilpatrick and Lott shows that the oxidation of tantalum metal in steam in the temperature range of 950–1300 °C follows a parabolic-linear (paralinear) rate law.[20] The oxidation has a rapid initial growth (at 119 °C, the Ta_2O_5 oxide grows rapidly until $t>7$ min) which obeys the parabolic law. The oxide growth then proceeds linearly. Whether the time dependence of the oxide growth on Ta-Si-N in wet ambient is parabolic for durations less than 5 min cannot be derived from our results. However, our observation of the rapid initial oxide growth is similar to the study by Kilpatrick *et al.*[20] This suggests that the rapid initial oxide growth is caused by Ta atoms on the film surface.

In summary, the oxide growth in the dry oxidation of the amorphous ternary Ta-Si-N alloy film is parabolic in time, and hence limited by the diffusion through the oxide. In wet ambient the oxide grows linearly with time with a fast initial rise. The same result has been reported for the wet oxidation of Ta metal.

V. CONCLUSIONS

Rf sputtered amorphous ternary $Ta_{36}Si_{14}N_{50}$ transforms to an amorphous $Ta_{14}Si_{5.5}O_{80}$ film after oxidations at 650–850 °C. The growth of the oxide follows a parabolic time dependence for dry oxidation between 700 and 850 °C and a linear time-dependence at 650 °C. The activation energies associated with the parabolic rate constant (dry oxidation) is 2.0 eV and that with the linear rate constant (wet oxidation) is 1.4 eV, respectively. 650 °C is observed to be a critical temperature for the dry oxidation mechanism: above that temperature the oxide growth is the limited by the diffusion through the oxide layer while at 650 °C the oxidation mechanism is reaction limited.

The wet oxidation is reaction limited and obeys a linear rate law. It also has a rapid initial oxide phase formation during approximately the first 5 min of oxidation.

According to our knowledge, this is the first published study on oxidation behavior of a ternary thin-film alloy so far.

ACKNOWLEDGMENTS

P. J. Pokela gratefully acknowledges a fellowship provided by the Academy of Finland. Also, we wish to thank the Finnish Culture Foundation and the Lohja Corporation for financial support. The authors are grateful to R. Gorris and B. Stevens for their technical assistance and R. Sampley for her contribution in manuscript preparation. The work was also partly supported by the U.S. Army Research Office and a grant from Intel Corporation.

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