

OXIDATION BEHAVIOUR OF LPCVD SILICON OXYNITRIDE FILMS

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In view of their application as oxidation masks in a modified LOCOS technology the oxidation behaviour of LPCVD silicon oxynitrides was investigated. In dry oxygen hardly any oxidation occurs. The oxidation rate increases with partial water pressure in the ambient. However, in any case the oxidation of oxynitride is at least one order of magnitude smaller than that of silicon. Layers with a composition near $O/N = 0.4$ were found to have the greatest oxidation resistance. The performance can be further improved by annealing the films prior to oxidation. A model is proposed in which the out-diffusion of N-containing reaction products limits the rate of oxidation. Hydrogen, originating from both the ambient and the as-deposited layer, plays a peculiar role in this process.

1. Introduction

The continuing demand for smaller dimensions in advanced IC designs requires a compact isolation scheme. A substantial reduction of the lateral encroachment of the field oxide (bird's beak) in the conventional LOCOS technique [1] is achievable when an oxynitride layer is used instead of the combination of silicon nitride and stress relief oxide [2]. This modified LOCOS technology is very attractive since it does not add any process step compared to the conventional scheme. For optimum performance deeper insight into the oxidation behaviour of oxynitride films may be useful.

In the literature a large amount of work has been published dealing with the oxidation of Si. Although there is general agreement that, apart from the initial stage, the rate of this process is determined by diffusion of oxidizing species to the reaction interface, opinions diverge as to the specific mechanism [3].

As regards silicon nitride oxidation, only a few quantitative studies have been documented for atmospheric-pressure CVD (APCVD) Si_3N_4 [4–6]. The kinetic data presented in these studies are indicative of a diffusion-controlled process, but no simple Deal–Grove behaviour is observed. Chramova et al. [6] have found that the oxidation rate decreases with decreasing hydrogen content of the nitride film. They have proved that the limiting process has to be related to the grown oxide layer rather than to the bulk of the nitride. Since extensive kinetic data for LPCVD oxynitrides were evidently lacking, we investigated the rate of oxidation at 1000°C for different SiO_xN_y film compositions. On the basis of the data collected in this study and of the results of a related study focusing on the role of hydrogen [7], a model is proposed for the oxidation of silicon oxynitride.

2. Experimental

Silicon oxynitride films were deposited at 820°C on Si(100) wafers applying the LPCVD process described before [8]. By tuning the $\text{NH}_3/\text{N}_2\text{O}$ input gas ratio the composition of the oxynitride films grown in this process can be varied at will. Thus, four series of oxynitride samples were prepared, with film compositions corresponding to an oxygen-to-nitrogen atomic ratio (O/N) of 0, 0.37, 0.69 and 1.02. Film thicknesses grown were about $400\text{ \AA}$ or $1000\text{ \AA}$. Oxidation runs were performed using a standard furnace in a clean room facility. An oxidation temperature of 1000°C was selected. The oxidation ambient was varied such that experiments under six different $\text{H}_2\text{O}/\text{O}_2$ flow ratios in the furnace were performed: $\text{H}_2\text{O}/\text{O}_2 = 0/100, 25/75, 50/50, 67/33, 75/25$ and $90/10$. In all runs the ambient contained 3% HCl.

Oxidations were carried out for 0.5, 1, 2, 4 and 9 h. The extent of oxidation was derived from RBS (Rutherford backscattering spectrometry) and ERD (elastic recoil detection) analysis of the samples. The experimental conditions have been described before [9,10]. These analytical techniques yield the absolute amount of N and O atoms per cm^2 and require no further calibration. By comparison with the as-deposited layer, the increase in the number of oxygen atoms due to oxidation, ΔO , is thus obtained. In general, the ERD and RBS results were found to agree very well, the differences found in ΔO typically being smaller than $5 \times 10^{15}\text{ atoms cm}^{-2}$.

3. Results

An overview of the results is given in figs. 1 and 2. The plots in fig. 1 reveal how the oxidation proceeds for the four different oxynitride compositions with ongoing reaction time. In general, oxynitride oxidation proceeds at a rate that

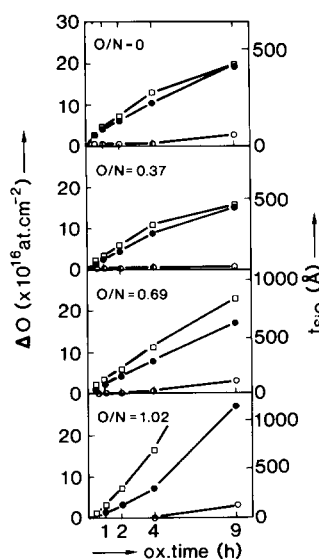


Fig. 1. Increase in oxygen content as measured after various oxidation treatments for the different oxynitride compositions. From the right-hand scale the grown oxide thicknesses can be read. Plotted are the results for three H₂O/O₂ ratios in the ambient: 0/100 (○), 50/50 (●) and 90/10 (□).

is at least one order of magnitude smaller than measured for the oxidation of silicon. To give an example: 9 h oxidation in a wet ambient (50/50) produces an oxide film of 1 μm on a reference Si wafer, compared with 450 $\text{\AA}$ on SiO_xN_y with O/N = 0.4. The shape of the curves is seen to change from

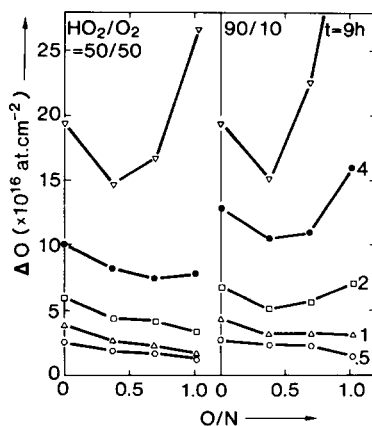


Fig. 2. Comparison of the performance of the different oxynitride compositions for two H₂O/O₂ ratios. For longer oxidation times an optimum is found near O/N = 0.4.

parabolic ($O/N = 0$ or 0.4) via linear ($O/N = 0.7$) to some higher order type of kinetics ($O/N = 1$). The oxidation resistance of oxynitride films is not greatly different from that of pure nitride. In fact, the results indicate that for $O/N = 0.4$ the oxidation proceeds even more slowly than for pure nitride ($O/N = 0$). When grown oxide thicknesses rather than ΔO values are compared (right-hand scale in fig. 1) the films with the two lowest O/N ratios are observed to perform similarly.

In all cases wet oxidation is faster than dry oxidation. In pure oxygen hardly any oxidation occurs. The effect of gas-phase composition seems to depend on oxynitride composition. The oxidation of pure nitride is accelerated when water is added to the ambient, up to an H_2O/O_2 ratio of 50/50. Further increase of the partial water pressure has no substantial effect. The same applies to the oxynitride having an O/N ratio of 0.4. In contrast, for $O/N = 0.7$ and $O/N = 1.0$ the rate of oxidation increases further when the H_2O/O_2 ratio is raised from 50/50 to 90/10.

For a given oxidation time the measured ΔO values can be compared for the different film compositions, as is worked out in the plots of fig. 2. For the shorter oxidation times (up to 2 h) the film composition does not seem to be a prominent parameter. For longer times, however, the results tend to diverge, especially for the larger H_2O/O_2 ratios. Oxynitrides in the composition range around $O/N = 0.4$ appear to have suffered least from oxidation.

4. Oxidation model

4.1. Rate-limiting step

The oxidation of a silicon oxynitride film may be conceived as a three-step mechanism: (1) transport of oxidant through the grown oxide to the oxidizing reaction front, (2) the actual oxidation reaction, and (3) transport of reaction products back to the solid-gas interface. In its simplest form the oxidation reaction may be written schematically as



The oxidation rates of oxynitrides are found to be much smaller than those of Si or SiO_2 . Since, to our knowledge, there is no evidence that the oxide grown on silicon is a material widely different from that formed by oxidation of (oxy)nitride, the first step of the process will be indistinguishable from OH_x diffusion through a conventional thermal oxide, and can therefore be precluded as being rate-limiting in the case of oxynitride oxidation. In view of the greater bond strength of Si-N as compared with Si-Si, the reaction rate in the second step may very well be lower than in the case of Si oxidation. As a result, the oxidation process may remain in its reaction-controlled regime for consider-

ably longer periods than observed for Si oxidation, and would show linear kinetics for longer reaction times and thicker grown oxides. The plots in fig. 1, however, are not very indicative of such a linear behaviour and most of the curves start to deviate clearly from linearity before a 500 Å thick oxide has formed. Also, the data published in the literature for APCVD Si_3N_4 oxidation have been interpreted in terms of a diffusion-controlled rather than a reaction-controlled process [4–6]. The shape of the curves in fig. 1 for $\text{O/N} = 0$ and 0.4 generally agrees with results published for Si_3N_4 . Thus, on the basis of these considerations the idea of rate limitation by reaction was abandoned.

This leaves the third step, out-diffusion of NH_x species, as the rate-limiting step. It implies that the diffusion of NH_x in SiO_2 is supposed to be considerably slower than that of OH_x . In order to explain all observations some further assumptions have to be made.

To start with, the results presented in figs. 1 and 2 show that wet oxidation proceeds faster than dry oxidation. This is also found for silicon oxidation, where the effect is ascribed to the one-order-of-magnitude larger permeation of water in silicon oxide compared to that of oxygen [11]. This effect may also play a role in the oxynitride oxidation. For wet ambients the concentration of H_2O in the grown oxide and at the oxidation interface will be larger than for dry ambients, just as with Si oxidation. As a result, the N-containing reaction products may be different from those formed in dry oxidations, e.g. the value of x in eq. (1) will be higher. Either the permeation of these H-rich NH_x products in SiO_2 is larger than that of H-poor species, or transport of any NH_x species is enhanced when more water is dissolved in SiO_2 . It is also conceivable that NH_x released at the interface is oxidized in the oxide to, say, NOH_x and that the rate of transport of this species to the outer surface is influenced by the water concentration in the oxide. Although we cannot discriminate between these possibilities yet, for our model it is sufficient to assume that the rate of out-diffusion of reaction products is enhanced by water.

4.2. *Role of hydrogen*

Although the model as worked out above may explain several trends observed for the oxidation of oxynitrides, it clearly needs further refinement since the differences in behaviour for various layer compositions cannot be explained yet. A related study of the hydrogen profiles in oxynitrides found evidence that hydrogen plays a role in the oxidation kinetics. As will be discussed in detail in a separate paper [7], a pile-up of hydrogen at or near the oxide/oxynitride interface was detected in oxidized samples. The contents of this H peak was found to be largest for the highest O/N ratios.

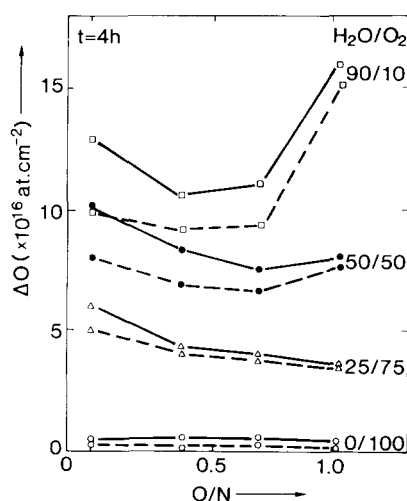


Fig. 3. Effect of a pre-anneal on the oxidation rate. Solid curves: as-deposited films; dashed curves: annealed for 1 h at 1000 °C in N₂ prior to oxidation.

Considering the oxidizing interface, the number of N atoms per cm² that has to be replaced by O atoms is smaller with increasing O/N. The ratio of NH_x species relative to OH_x species (eq. (1)) may therefore vary not only with H₂O/O₂ ratio in the ambient, but also with O/N ratio of the solid. This NH_x/OH_x ratio at the interface may in turn determine the composition of the species to be transported to the outer surface. This is in agreement with our observation that the size of the H pile-up at the interface increases with O/N ratio [7].

A second source of hydrogen may be the oxynitride layer itself. In a previous investigation we have established that a substantial part of the hydrogen, incorporated in oxynitride layers during deposition, desorbs in a subsequent anneal treatment at 1000 °C [12]. An initial hydrogen content of 3 at% in the as-deposited layer is reduced to 0.6 at% or less upon annealing in an ambient free of hydrogen. In fig. 3 the oxidation behaviour of as-deposited films is compared with that of films that had been annealed at 1000 °C prior to oxidation. This plot shows that a pre-anneal results in some reduction of the oxidation rate, but again this is not equal for all compositions: the larger the O/N ratio the smaller the improvement in oxidation resistance. It is feasible that the oxidation process is affected primarily by the desorption of N-bonded hydrogen. This type of desorption will be largest for the N-rich oxynitride compositions, which might explain the observations in fig. 3.

The peculiar role of hydrogen in the oxidation of oxynitride is further demonstrated by the behaviour in dry oxygen (H₂O/O₂ = 0). The plots in fig. 1 show that hardly any oxidation occurs under this condition. (The slight

oxidation found for $t = 9$ h may have been caused by residual water.) Fig. 3 indicates that the slight oxidation in dry oxygen can be nearly completely suppressed by a pre-anneal at 1000°C . In dry oxidation the only source of hydrogen is the oxynitride layer itself. In the first 30 min of oxidation most of this hydrogen will desorb into the ambient. A fraction of this amount will be involved in an oxidation reaction according to eq. (1), giving rise to a slight oxidation of a surface region. Since no additional hydrogen is supplied from the dry ambient, the oxidation of the layer will terminate.

5. Conclusions

The results presented in this paper show that the oxidation behaviour of LPCVD oxynitride layers is quite complex. The oxidation rates measured are at least one order of magnitude smaller than those found for Si oxidation under identical conditions. Oxynitrides with a composition ratio in the range $0 \leq \text{O/N} < 0.5$ show better oxidation resistance than the oxygen-rich films, with an optimum near $\text{O/N} = 0.4$.

In dry oxygen the films hardly oxidize at all, irrespective of oxynitride composition. The differences between the various compositions are distinct in wet ambients and for longer oxidation times. The oxidation resistance can be further improved by annealing prior to oxidation. Such an anneal has the greatest effect for pure nitride, where the hydrogen desorption is largest. The out-diffusion of N-containing oxidation products is most likely the rate-limiting step. In addition, hydrogen plays a role in the oxidation kinetics: transport of N-containing products to the outer surface is enhanced by adding water to the oxidizing ambient. This may result from a larger permeation of these products when water is dissolved in silicon oxide, or from the formation of faster diffusing species by reaction with OH_x .

We found evidence for an accumulation of hydrogen species near or at the oxidizing interface during oxidation. The extent of accumulation varies with layer composition [7], which may be the key feature in interpreting the oxidation kinetics of LPCVD oxynitrides.

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