PHYSICAL REVIEW B VOLUME 48, NUMBER 8 15 AUGUST 1993-II

Dynamic behavior of hydrogen in silicon nitride and oxynitride films made by low-pressure chemical vapor deposition

W. M. Arnoldbik, C. H. M. Marée, A. J. H. Maas,* M. J. van den Boogaard, and F. H. P. M. Habraken
Department of Atomic and Interface Physics, Debye Institute, University of Utrecht, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

A. E. T. Kuiper
Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands
(Received 24 March 1993)

The diffusion and reactivity of hydrogen, incorporated in silicon oxynitride films during low-pressure chemical vapor deposition (LPCVD) at 800 °C, has been studied using elastic recoil detection and infrared spectroscopy for temperatures ranging from 700 to 1000 °C. The experiments are based on the determination of the hydrogen and deuterium depth profiles in layer structures in which H and D have been incorporated in different layers. This was achieved in two ways. Double layers have been produced directly during deposition or through exchange of incorporated hydrogen with gas-phase deuterium. The diffusion coefficient of hydrogen (or deuterium) is in the range between 3×10^{-18} and 1×10^{-13} cm^2/s, at temperatures between 700 and 1000 °C, and is characterized by a single activation energy of 3 eV, for [O]/([O]+[N]) values up to 0.45. The diffusion coefficient and hence the rate of the exchange of incorporated hydrogen and gas-phase deuterium increases with [O]/([O]+[N]) in the oxynitrides for [O]/([O]+[N]) $>$ 0.3. As a result we propose a model in which the rate-limiting step in the process of the diffusion of hydrogen in the LPCVD oxynitrides is the breaking of N-H bonds. Subsequent to the bond breaking, the hydrogen atom becomes trapped in a nitrogen-related trapping site or exchanges with a nitrogen-bonded hydrogen (deuterium) atom. If the bond breaking occurs within a distance of about 10 nm from the immediate surface, the hydrogen atom is able to desorb into the gas phase. A SiO_2 capping layer is not able to prevent the desorption.

I. INTRODUCTION

Currently there is considerable interest in the dynamic behavior of hydrogen in silicon-related amorphous semiconductors and insulators.[1–3] This interest stems from two interconnected considerations. First, the presence of hydrogen in these materials is a major cause of their instabilities, because of its capability to diffuse in these materials at relatively low temperatures. Second, since defects in these materials play a decisive role in their applications and since hydrogen and defect physics have been found to be closely related, the study of the hydrogen dynamic behavior may reveal important information about the defect physics in such amorphous semiconductors and insulators. Next to this general interest, hydrogen plays an important role in Si-O-N-H based materials, because it facilitates chemical reactions to occur in this reaction system at relatively low temperatures.[4]

Deposited silicon nitride and oxynitride films find their most important applications in silicon-based very large scale integrated (VLSI) isolation technology. The performance of the silicon nitride and oxynitride films in (the manufacturing of) integrated circuit devices is related to the role hydrogen plays in the physical chemistry in these materials.[5,6] During low-pressure chemical vapor deposition (LPCVD) of silicon nitride and oxynitride, hydrogen is incorporated in both N-H and Si-H bonds to concentrations of 2–10 at. %.[7–9] The incorporated hydrogen desorbs from the films when they are annealed at temperatures above the deposition temperature in vacuum or inert-gas ambients. This process is reversible: hydrogen can to some extent be reintroduced when a subsequent anneal takes place in a H_2 ambient. This process of release and reintroduction of hydrogen parallels the flat band voltage shifts in metal-nitride-oxide-semiconductor structures.[8,10–12]

It has been found that for LPCVD silicon oxynitride films the rate of hydrogen loss shows a minimum for an oxygen-to-nitrogen [O]/([O]+[N]) concentration ratio of about 0.3. At this composition the hydrogen content in the as-deposited material tends to be maximum.[9] It is conceivable that this maximum is somehow related to the above desorption process, as this process is likely to be operative during deposition. This then would have important consequences for the [O]/([O]+[N]) dependence of the electrical properties of oxynitride films in their as-deposited state.

For the thermal oxidation of silicon nitride, hydrogen plays a crucial role in inducing the conversion of silicon nitride to silicon dioxide at moderate temperatures.[4,13] It has been shown that hydrogen piles up at the oxide/(oxy)nitride interface. The total contents and the width of this interfacial hydrogen distribution increase

 ©1993 The American Physical Society

with increasing [O]/([O]+[N]) concentration ratio in the oxynitride film.[14]

For a better understanding of all above-mentioned observations, a deeper insight in the processes of incorporation, diffusion, and desorption of hydrogen and their [O]/([O]+[N]) dependence in oxynitrides is a prerequisite. In this paper we describe experiments to unravel the mechanisms of hydrogen incorporation from the gas phase, hydrogen motion in the oxynitride, and hydrogen removal from the surface region of these films. We consider the [O]/([O]+[N]) ratio in the LPCVD oxynitride films as an important parameter.

In the experiments use has been made of the isotope sensitivity and of the depth resolving power of the high-energy ion-beam technique of elastic recoil detection.[15] Incidentally also (Fourier transform) infrared absorption spectroscopy has been applied.

II. EXPERIMENT

A. Samples

Several series of LPCVD silicon oxynitrides films were deposited onto silicon wafers in a conventional horizontal hot wall reactor. Oxynitrides were grown from SiH_2Cl_2, N_2O, and NH_3.[16] The gas flow ratio $[NH_3(ND_3)+N_2O]/[SiH_2Cl_2]$ was kept constant at 3. The [O]/([O]+[N]) solid-state concentration ratio was varied between 0 and 0.5 by variation of the $[N_2O]/[NH_3]$ gas flow ratio. In addition, double layers were produced of oxynitrides grown subsequently from NH_3 and ND_3. Also the reverse order was applied.[17] In each double-layer structure the [O]/([O]+[N]) ratio in the two sublayers was very similar. For further details see Table I. These structures were deposited onto *p*-type *c*-Si substrates.

Samples having a NH_3 layer on top of a ND_3 layer are denoted by HD. DH denotes the reversed structure. The NH_3 layer and the ND_3 layer in each structure were about equally thick. Double-layer structures were annealed at temperatures ranging from 700 up to 1000 °C for periods between 1 min and 7 days.

Single-layer structures were produced in two similar series,[16,18] as identified in Table II.

These samples were annealed in a 4% D_2-N_2 mixture for 5 min at 800 °C, for 5, 20, and 60 min at 900 °C or for 5 min at 1000 °C. Part of each sample was preannealed for 1 h at 1000 °C in argon. The history of the samples will be indicated by the addition of the prefixes AD (as-deposited) and PA (preannealed) to the identification code.

Silicon nitride layers, grown from ND_3 as thin as 5 nm, have been deposited on *c*-Si wafers in order to study in more detail the surface desorption process. For the same purpose also some of the DH double-layer samples were covered with a 50-nm-thick SiO_2 layer grown from TEOS (tetraethylorthosilicate).

B. Analysis

Hydrogen and deuterium concentration depth profiles were determined using elastic recoil detection (ERD). In these measurements we employed a 10-MeV ^{28}Si ion beam from the Utrecht University tandem accelerator. A conventional setup was used; a stopper foil of 6 μm thickness was placed in front of a silicon surface barrier detector to stop all heavy primary and recoil particles.[17] The Si ion-beam dose was determined by the measurement of the Si backscattering yield of Au covered carbon blades, which periodically intercepted the beam.

The recoil and the incidence angles (with respect to the surface normal) amounted to 33° and 28°, respectively. This choice of ion-beam energy and configuration minimizes interference of the hydrogen and deuterium spectral features for the single as well as double layers, preserving a good depth resolution.

At the surface the depth resolution amounted to about 5 nm. It is estimated to be 10 nm at a depth of 100 nm. In these measurements the stopping powers of both incoming and outgoing particles vary only slightly over the depth of the layer structure and are therefore taken as constant. The energy scale of the ERD spectra can hence easily be converted into a depth scale. After correction for the variation in the recoil cross section with energy, the concentration depth profiles of H and D in the layers are obtained.

The overall composition and thicknesses of the layers were established using ERD, employing a 30-MeV ^{28}Si ion beam and a 9-μm foil, and by means of Rutherford backscattering spectrometry. Fourier-transform infrared spectroscopy (FTIR) measurements were performed to obtain information concerning the type of H bonds in the samples. We used a Biorad FTS40 spectrometer equipped with a LN_2-cooled MCT detector.

TABLE I. Identification code, [O]/([O]+[N]), and thickness of LPCVD double layers.

Sample	[O]/([O]+[N])	Thickness top layer (nm)	Thickness bottom layer (nm)	Total thickness
HD0	0.00	60	90	150
HD3	0.21	89	89	178
HD5	0.32	98	85	183
HD8	0.45	93	87	180
DH0	0.00	75	75	150
DH3	0.21	89	99	188
DH5	0.32	85	95	180
DH8	0.45	87	85	172

TABLE II. Identification code, [O]/([O]+[N]), and thickness of LPCVD samples (single layers).

Sample	[O]/([O]+[N])	Thickness (nm)
I1	0.00	78
I2	0.19	76
I3	0.24	72
I4	0.33	71
I5	0.49	85
P1	0.00	127
P2	0.22	134
P3	0.38	146
P4	0.42	138
P5	0.50	103

The amount of deuterium plus hydrogen found in the layers and its dependence on the [O]/([O]+[N]) concentration ratio agree with previous measurements.[9,18]

III. DIFFUSION OF HYDROGEN IN SILICON OXYNITRIDE FILMS: DOUBLE-LAYER EXPERIMENTS

The FTIR measurements on single layers of ND_3 oxynitrides indicated that the majority of D is bonded to nitrogen. Apart from an absorption in the region of 2200 cm^{-1}, attributed to Si-H bonds, the spectra show small absorption features at 1600 cm^{-1}, attributed to Si-D, and at 3350 cm^{-1}, attributed to N-H bonds. This indicates that during deposition some isotope exchange has occurred, probably at the growth surface.

Figure 1 shows the H and D concentration profiles of the silicon nitride double layer having the NH_3-grown layer on top (HD0), after annealing at 1000 °C for various periods. The positions of hydrogen and deuterium at the surface and at the interface are indicated. Hydrogen is shown to be present in a low concentration in the ND_3-grown layer of the as-deposited sample, i.e., at a depth between 90 and 150 nm. This hydrogen originates from the SiH_2Cl_2 gas component during deposition. The concentration profiles reveal that during annealing interdiffusion of H and D is taking place at the interface between the two nitride layers.

Figure 2 shows how the total amount of deuterium decreases with anneal time. The results of the reversed structure (DH0) are included. It appears that the deuterium content of DH0 starts to decrease immediately after the start of annealing. In contrast, when D is present in the bottom layer only (HD0), the total amount of deuterium in the sample starts to decrease only after 4 min of annealing. From the concentration depth profiles of Fig. 1 it can be seen that this period of 4 min is about equal to the period necessary for D to diffuse from the lower layer to the surface in measurable amounts. Using FTIR we did not observe a reduction of the number of N-D bonds in the samples which were annealed shorter than this period. In the samples with other [O]/([O]+[N]) ratios we noted a similar correspondence between the desorption of

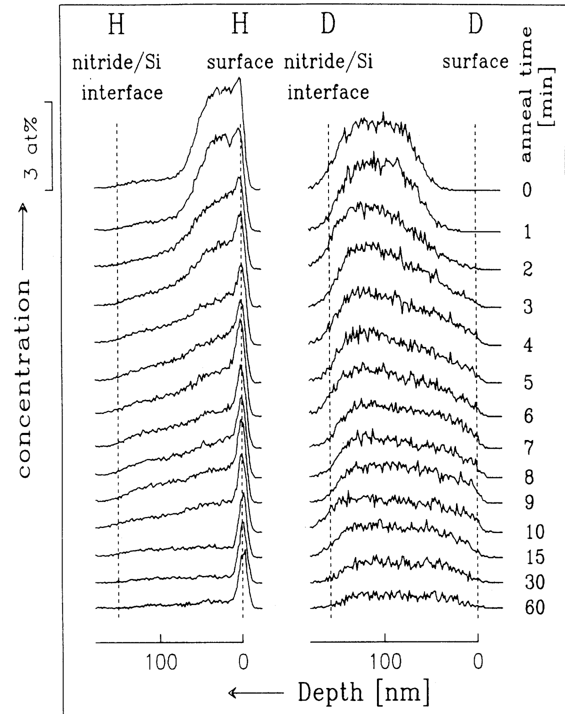


FIG. 1. Hydrogen and deuterium concentration depth profiles of the silicon nitride sample having the ND_3 layer below the NH_3 layer (HD0), during annealing at 1000 °C. Anneal periods are indicated at the right-hand side of each curve.

the deuterium and its presence in the immediate surface layer. The behavior of hydrogen is analogous to that of deuterium, but less pronounced, since it is also present in the ND_3 layers and thus starts to decrease at the onset of annealing in either layer structure.

Combination of Figs. 1 and 2 and the FTIR data leads

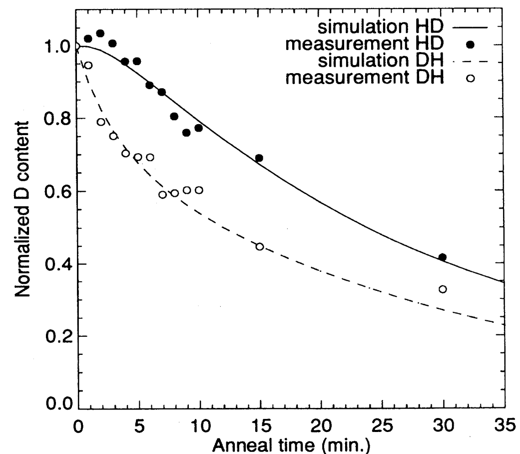


FIG. 2. Total deuterium content of the samples HD0 and DH0 vs annealing time at 1000 °C. The drawn lines denote simulations of the process of diffusion and desorption as is discussed in Sec. V A.

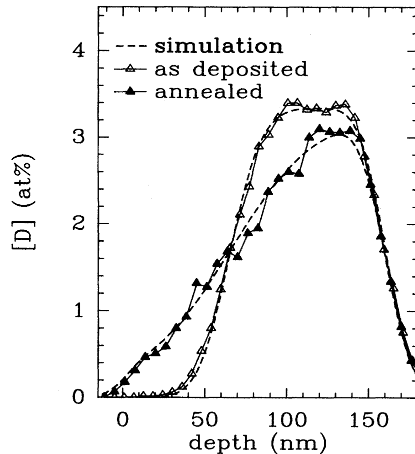


FIG. 3. Simulated and measured deuterium depth profile of HD0, as-deposited and after annealing for 3 min at 1000 °C.

to the conclusion that release of hydrogen from LPCVD Si_3N_4 and oxynitride proceeds through the diffusion of bonded hydrogen to the surface followed by desorption. Furthermore, hydrogen (or deuterium) diffusion into the crystalline Si substrate is not occurring to a substantial extent, in contrast to what has been supposed earlier.[19]

The concentration depth profiles were compared with computer simulations of Fick-type diffusion in order to determine the diffusion coefficient (see the Appendix). The simulations were adjusted taking the finite depth resolution into account. A χ^2 analysis established the best-fitting diffusion coefficient for each profile. The simulations were performed for the deuterium concentration profiles of the structures having the NH_3 layer on top and for anneal times such that the deuterium did not reach the surface. The influence of the presence of the surface on the concentration profiles and a possible influence of the concentration on the diffusion coefficient was minimized in this way. The hydrogen concentration profiles were not used, because the presence of hydrogen in the ND_3 layer would make the analysis much more complicated. However, inspection of the H and D profiles (Fig. 1) and H+D (not shown) concentration profiles indicates that the behavior of H and D must be very similar.

Figure 3 shows that very good agreement between the measured and simulated profiles is obtained. The thus determined diffusion coefficient $\mathcal{D}$ is plotted versus [O]/([O]+[N]) in Fig. 4. The diffusion coefficient shows a pronounced minimum in the range [O]/([O]+[N])=0.2–0.4. It varies between 3×10^{-18} and 1×10^{-13} cm^2/s, in the temperature range between 700 °C and 1000 °C. The diffusion coefficient appears to depend exponentially on reciprocal temperature over the entire temperature range of this study, as is shown in Fig. 5. This indicates that everywhere in this temperature range the same step is rate limiting. The activation energy does not vary significantly with [O]/([O]+[N]) and amounts to about 3.0 eV.

The deuterium profile in the as-deposited nitride agrees, according to the simulations, with a step-function concentration profile annealed for about 20 min at 800 °C. This period is close to the total time the structure was subjected to a temperature of 800 °C during the process of deposition of the upper layer.

The value that we find for the activation energy of bulk diffusion of bonded deuterium is significantly larger than the value published previously by Schols and Maes for hydrogen diffusion.[20] Their experiment has generated the apparent activation energy of the diffusion rate in a rather indirect manner, viz. from the incorporation of hydrogen from the gas phase. The observed activation energy in that study may be the result of mixing up of two steps, i.e., incorporation and diffusion.

Since the value for the activation energy, determined here, is close to the N-H bond energy,[21] we suppose that in the diffusion process the breaking of N-H bonds is the rate-limiting step and diffusion proceeds through exchange of (mainly N-) bonded hydrogen and deuterium. In this picture the mobile species is a nonbonded hydrogen (deuterium) atom.

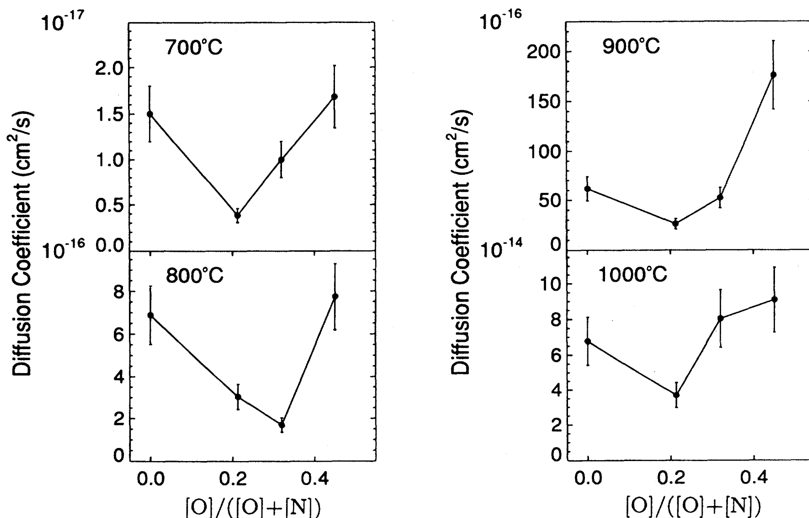


FIG. 4. The diffusion coefficient $\mathcal{D}$ of deuterium in the double layers at 700 °C, 800 °C, 900 °C, and 1000 °C, vs [O]/([O]+[N]).

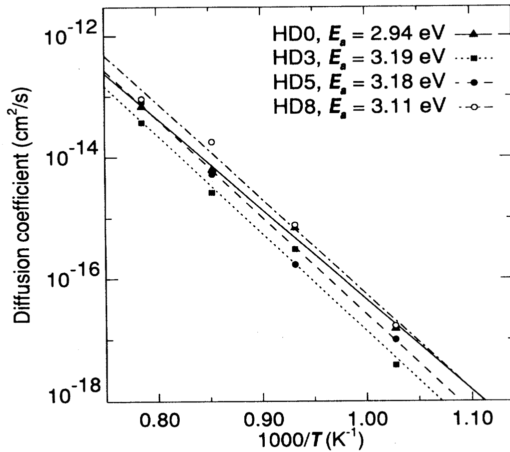


FIG. 5. Arrhenius plot of the diffusion coefficient $\mathcal{D}$ of deuterium in the double-layer samples. For the sample identification code: see Table I.

IV. DEUTERIUM UPTAKE AND HYDROGEN LOSS DURING ANNEAL IN D_2-N_2

A. Results

With the small layer thicknesses used, the amounts of hydrogen and deuterium in our samples are below or close to the detection limit of the Fourier-transform infrared absorption spectrometer used. Nevertheless, ir measurements of the as-deposited hydrogen-containing samples show that in these oxynitrides hydrogen is mainly bonded to nitrogen. A fraction of 20–30 % is incorporated in SI-H bonds which disappear completely during the anneal treatments. After D_2-N_2 annealing we observe an absorbance peak in the region of 2500 cm^{-1}, which is indicative of the presence of N-D bonds. We were not able to detect an Si-D peak. We therefore conclude that the Si-D concentration is small.

Figure 6(a) shows the total amount of D incorporated in the as-deposited oxynitrides as a function of [O]/([O]+[N]) for the various D_2-N_2 anneal temperatures. For [O]/([O]+[N])<0.3 the amount of D incorporated is on the order of 10^{15} atoms/cm^2, for all considered anneal temperatures. It has a minimum at [O]/([O]+[N])=0.2, for all temperatures, but increases strongly for [O]/([O]+[N])>0.3. The extent of D incorporation increases with increasing temperature.

During the D_2-N_2 anneal of the as-deposited samples, hydrogen incorporated during deposition, leaves the oxynitride films. This hydrogen loss is plotted as a function of [O]/([O]+[N]) in Fig. 6(b). At the higher anneal temperatures the amount of desorbed hydrogen has a minimum around [O]/([O]+[N])=0.2. The coinciding minima in the amount of released hydrogen and incorporated deuterium at [O]/([O]+[N])=0.2 are consistent with the earlier observed maximum stability of H in the material at this particular composition.[9] The total amount of hydrogen desorbed from the films is significantly larger than the amount of D incorporated if the anneal is at a temperature of 1000 °C [see Fig. 6(c)].

Figure 7 shows the number of deuterium atoms incorporated in the preannealed oxynitrides, during a 5-min anneal in D_2-N_2 at 800, 900, and 1000 °C. During the D_2-N_2 anneal the PAI samples incorporate only 10–50 % of the amount of deuterium that is incorporated in the ADI samples. We explain this by assuming that during the high-temperature pre-anneal step a part of the Si and N bonding sites for H (or D) is annihilated by cross-linking.[18] Still, both in the ADI and in the PAI material the deuterium uptake starts to increase at [O]/([O]+[N]) ratios above 0.25. However, in the PAI samples no distinct minimum around [O]/([O]+[N])=0.2 can be observed.

Figure 8 shows ERD deuterium concentration depth profiles of ADI3 and PAI3 ([O]/([O]+[N])=0.24) and of ADI5 and PAI5 ([O]/([O]+[N])=0.49), after annealing for 5 min at 900 °C in D_2-N_2. These profiles again show that the extent of D uptake in the I3 samples is much smaller than in the I5 samples. Furthermore, in the I3 samples, the presence of D is confined to a thin layer at the surface, whereas in the I5 samples deuterium appears to be distributed over the entire depth of the film. This leads to the conclusion that the diffusion coefficient of D in ADI3 and PAI3 is smaller than in ADI5 and PAI5.

In Fig. 9, the concentration depth profiles of deuterium and hydrogen in all ADI and PAI samples are shown, after annealing at 900 °C for 5 min in D_2-N_2. Also the summation of these profiles is plotted as well as the hydrogen depth profile recorded before the D_2-N_2 anneal. The plots suggest that all H released during the D_2-N_2 anneal is replaced by D; the small differences between the

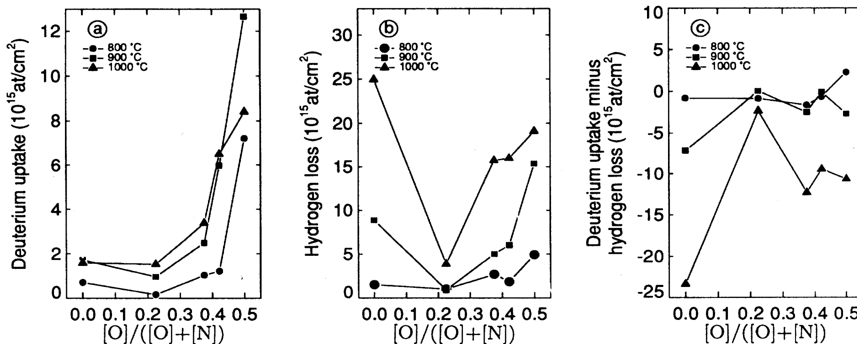


FIG. 6. (a) Total deuterium uptake, (b) hydrogen loss, and (c) the difference between these quantities in LPCVD silicon oxynitride films during annealing for 5 min in a 4% D_2-N_2 mixture at the indicated temperatures, vs [O]/([O]+[N]).

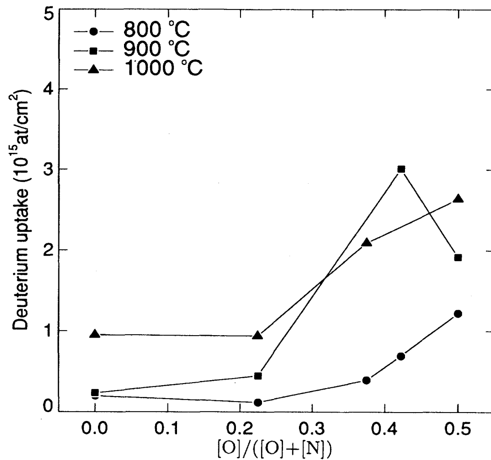


FIG. 7. Total amount of D incorporated in preannealed silicon oxynitride films vs [O]/([O]+[N]) during annealing for 5 min in a 4% D_2-N_2 mixture at the indicated temperatures. The loss of hydrogen during the anneal of the preannealed samples equals the deuterium uptake.

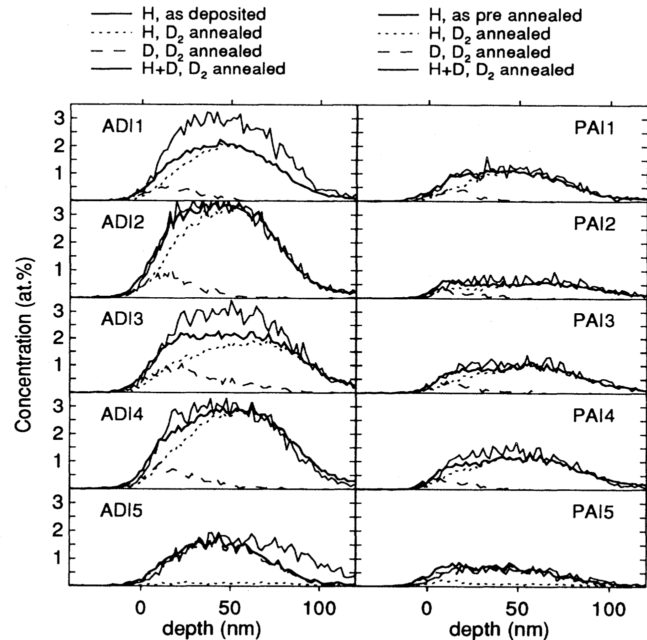


FIG. 9. The concentration depth profiles of hydrogen and deuterium of the ADI and the PAI samples after a 5-min D_2-N_2 anneal at 900 °C. Also plotted is the summation of these profiles, as well as the hydrogen depth profile prior to the D_2-N_2 anneal. The identification codes of the samples are indicated.

solid curves in the ADI profiles point to some additional cross linking [cf. Fig. 6(c)]. Not in a single case is a local H+D concentration found that is larger than the local H concentration prior to the D_2-N_2 anneal. After annealing at 1000 °C (not shown) a net loss occurs only in the as-deposited material, but not (within the experimental accuracy) in the preannealed samples.

The amounts of D in the oxynitride films as a function of the anneal period at 900 °C are shown in Fig. 10. The data suggest that the D incorporation obeys a $\sqrt{t}$ law.

B. Discussion

In the LPCVD silicon oxynitride films hydrogen is present in both Si-H and N-H bonding configurations. However, the N-H bonds strongly outnumber the Si-H bonds.[9,7] Therefore, we will focus only on the N-H groups in the discussion of the observations. This is the more justified by the observation of only Si-N-D bonding in the D_2-N_2 annealed films.

The incorporation of D in the LPCVD oxynitrides during the anneal treatment is conceived as a two-step process, i.e., diffusion of deuterium species into the material and exchange of bonded H with D. In similar measurements for plasma-deposited (PECVD) silicon oxynitride films we have been able to deduce that the first step in the process is the bonding of D in the surface region of the sample. The subsequent step is the diffusion of the bonded D from this surface region deeper into the film.[22]

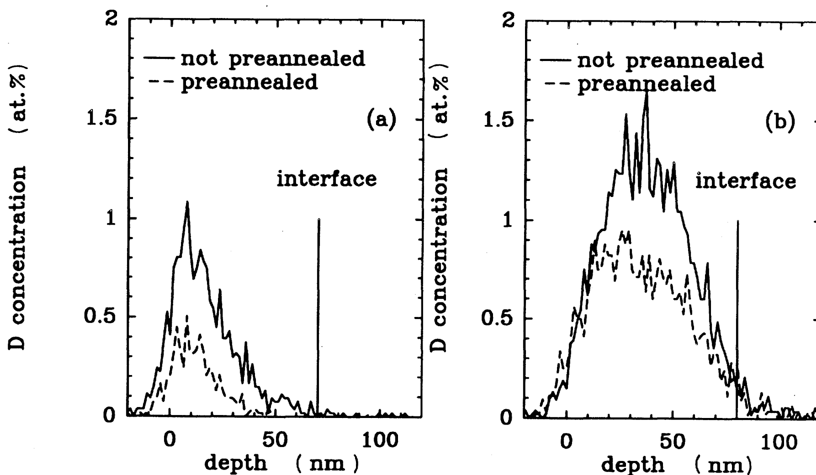


FIG. 8. Deuterium concentration depth profiles as-obtained by ERD for the as-deposited and preannealed silicon oxynitride films with (a) [O]/([O]+[N]) = 0.24 and (b) [O]/([O]+[N]) = 0.5 before and after annealing at 900 °C for 5 min.

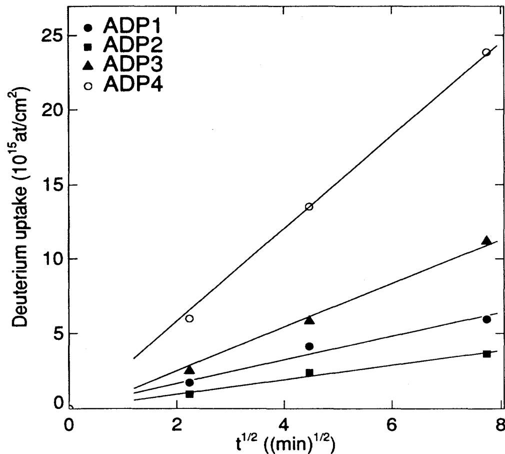
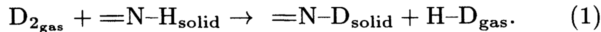


FIG. 10. Total amount of deuterium incorporated in LPCVD silicon (oxy)nitride films of various compositions, as a function of the square root of the annealing time at 900 °C in D_2-N_2. For the sample identification code: see Sec. II A and Table II.

For the PECVD samples we have been able to study the surface reaction distinctly from the diffusion process since in the as-deposited PECVD oxynitride films the diffusion rate appeared very large. Further, in the measurements of D uptake in PECVD material the concentration of =N–D groups in the surface region was such low that it did not significantly lower the uptake rate. From the D incorporation rate in the PECVD material we have deduced an activation energy of 1.5 eV. We assume this step to proceed according to the exchange reaction[22,23]



$$D_{2_{gas}} + {=}N\text{–}H_{solid} \rightarrow \; {=}N\text{–}D_{solid} + H\text{–}D_{gas}. \quad (1)$$

In the case of the LPCVD samples of this study, the situation is more complex. We never have observed a H+D concentration that was larger than the initial hydrogen concentration. This strongly suggests that the number of sites available for D is at most equal to the initially present H bonds. Although the extent of D incorporation is rather small (see Figs. 6 and 7), the D surface concentration cannot be neglected compared to the hydrogen concentration (and thus compared to the concentration of available bonding sites). The decrease of the number of =N–H bonds available for exchange during the anneal treatment causes the rate of uptake of D to decrease with reaction time. As a consequence, the diffusion of D from the surface deeper into the solid becomes rate limiting after a (brief) period (see Fig. 10). If the amount $M(t)$ of D incorporated during a period of time t is determined by a constant surface D concentration C_s and a diffusion coefficient $\mathcal{D}$, while D has not yet reached the interface of the film with the substrate, it holds that[24]

$$M(t) = 2C_s\sqrt{\frac{\mathcal{D}t}{\pi}}. \quad (2)$$

The data presented in Fig. 10 indicate indeed that the product $C_s\sqrt{\mathcal{D}}$ depends on the [O]/([O]+[N]) ratio but not on the time t. We have fed the values of the diffusion coefficients, as determined in Sec. III, in Eq. (2) and calculated the D surface concentrations C_s during the anneal treatment. The values thus derived from the data given in Fig. 10 are presented in Fig. 11. For [O]/([O]+[N]) concentration ratios lower than 0.3, C_s amounts to about 1 $\times 10^{21}/\text{cm}^3$ or 1 at. %. For larger [O]/([O]+[N]) ratios C_s is larger. Figure 11 also shows the values for C_s for the other temperatures (Fig. 6) and for the preannealed samples. Note that the values of C_s for 800 °C and 900 °C coincide. For the samples (pre-)annealed at 1000 °C C_s is smaller, but again it increases with [O]/([O]+[N]) for [O]/([O]+[N])> 0.3.

Having established the kinetics of D uptake we now can again determine the diffusion coefficients from the measured D profiles in this series of experiments. We determined the diffusion coefficient of D in both the ADI and the PAI samples from the measured D profiles using the approach as described in the Appendix. In this estimation we assumed that the concentration

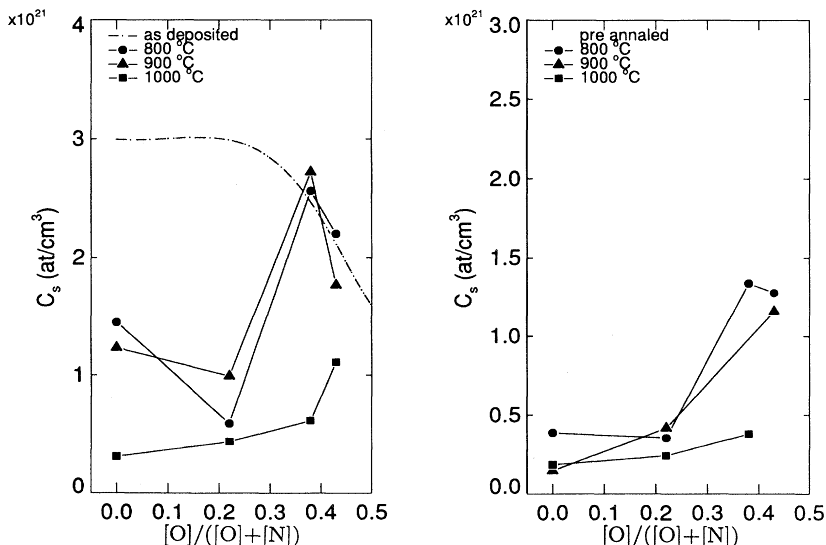


FIG. 11. C_s vs [O]/([O]+[N]). Also plotted is the hydrogen concentration of as-deposited LPCVD silicon oxynitride (Ref. 9).

of the deuterium in the surface layer is constant with reaction time and assume this layer infinitely thin. As visible in Fig. 9, deuterium atoms in the samples with the largest [O]/([O]+[N]) ratio reach the interface, thus prohibiting the determination of the diffusion coefficient of these samples according to the method above. The same holds for the samples annealed at 1000 °C in D_2-N_2. The samples annealed at 800 °C revealed ERD D spectral features which are only slightly broadened compared to the depth resolution. Therefore, the resulting values for $\mathcal{D}$ are very inaccurate. Hence we only present the values of $\mathcal{D}$ for 900 °C in the as-deposited and the preannealed samples (Fig. 12). These values are in good agreement with the values determined from the double-layer experiments (Sec. III). Again, these experiments point to a minimum $\mathcal{D}$ at [O]/([O]+[N]) ratios of about 0.2–0.3. For [O]/([O]+[N])=0 there may be a small decrease of $\mathcal{D}$ as a result of preannealing. Qualitatively, this decrease has also been found for other D_2-N_2 anneal temperatures. The determination of $\mathcal{D}$ in the preannealed material could never have been obtained from the double-layer experiments.

The minimum diffusion rates found at [O]/([O]+[N]) = 0.2–0.3 explain qualitatively the minimum uptake of D in this [O]/([O]+[N]) range. At the same time, the evolution of the diffusion coefficient at larger [O]/([O]+[N]) ratios explains the strong increase in D uptake at [O]/([O]+[N]) ratios above 0.2.

We conclude that the [O]/([O]+[N]) dependence of the rate of uptake of D from the gas phase is controlled by the rate of diffusion of bonded deuterium from the surface region deeper into the (oxy)nitride film. Further we note that the [O]/([O]+[N]) dependence of C_s is similar to that of $\mathcal{D}$. This is consistent with a model in which the diffusion of D is a consequence of a D-H exchange process (see Sec. VI). In this view the uptake of D proceeds because the indiffusion of D leaves the surface with N-H sites, capable to exchange with D from the gas phase.

The observation that the diffusion rate in the lower [O]/([O]+[N]) oxynitrides is smaller in the preannealed samples than in the as-deposited samples is consistent

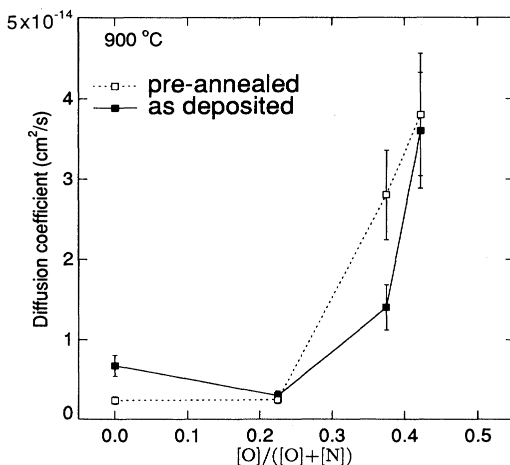


FIG. 12. The diffusion coefficient $\mathcal{D}$ at 900 °C vs [O]/([O]+[N]) for the as-deposited and preannealed samples.

with the observation that the total D uptake is smaller in the preannealed samples. In addition, the total uptake of D is determined by the number of available sites. This number is supposed to be reduced during the 1000 °C pre-anneal step.

During the D_2-N_2 annealing H is lost from the film. At an anneal temperature of 800 and 900 °C the amount of H lost is about equal to the amount of D taken up [see Fig. 6(c)]. At 1000 °C, however, the loss of H is larger than the uptake of D. Apparently, there are two routes for H loss, one of which is the exchange reaction with D. This process dominates in our conditions at the lower temperatures. The other process must be a process which is accompanied by a removal of H (D) bonding sites, and must have an appreciable rate at 1000 °C. This is inferred from the observation that in the preannealed samples C_s and the D content do not approach the values reached in the as-deposited samples. We suppose that the removal of D or H bonding sites occurs through formation of additional Si-N bonds and/or N-N bonds as a consequence of cross linking.[18,25,26]

This process leads to a loss of N-H bonds and N- and Si-related bonding sites, reinforcing that the D incorporation takes place essentially in N-D groups. In the PA samples the only route for hydrogen loss is the exchange with D, since the other process occurred already during the 1000 °C preanneal. In the oxynitride with [O]/([O]+[N]) $\approx$ 0.2–0.3 the process of removal of hydrogen without exchange with deuterium apparently has a lower rate compared to the other oxynitride compositions studied [Fig. 6(c)].

The observation that at temperatures between 800 and 900 °C C_s is independent of the anneal temperature implies that in this temperature region the apparent "activation energy" of $M(t)$, as determined from the slope of a plot of $\ln M(t)$ vs reciprocal T, is half the value for the activation energy of $\mathcal{D}$ [see Eq. (2)]. Such an evaluation indeed results in an apparent activation energy of $M(t)$ for 800 and 900 °C of 1.4 eV. The 1000 °C samples do not fit in this analysis since C_s at 1000 °C is lower than at the other temperatures, but also because at 1000 °C $\mathcal{D}$ decreases for low [O]/([O]+[N]) values (cf. Fig. 12) and because D reaches the interface for the larger [O]/([O]+[N]) samples.

The deduced values of C_s at 800–900 °C are lower than the as-deposited hydrogen concentration for the lower [O]/([O]+[N]) ratios (see Fig. 11). These lower values may be the result of an equilibrium between the rates of incorporation in the surface region, of diffusion from this region deeper into the film, and of desorption from this surface layer into the ambient (see Sec. V B). The apparent activation energies for the two processes of the initial uptake and of the diffusion are about equal: the activation energy for the incorporation reaction has been found to amount to about 1.5 eV (Ref. 22) whereas the transport of D deeper into the film is characterized by an activation energy of half that of $\mathcal{D}$ [i.e., the time derivative of $M(t)$, with C_s constant; see Eq. (2)]. The equality of the two activation energies might consistently explain the independence of C_s on the anneal temperature. However, this reasoning makes it implausible that the surface

concentration is constant with reaction period (or, stated differently, with extent of total D incorporation). If, however, the equilibrium between incorporation and desorption determines the C_s, then it is difficult to conceive that the 800 and 900 °C values are about equal in view of the difference in activation energy for the processes of incorporation and desorption (see Sec. V B).

A different approach might be to suppose that the values deduced for C_s are saturation values, i.e., the maximum D concentration which can be accommodated in the material from the gas phase. Indeed for the larger [O]/([O]+[N]) ratios C_s approaches the as-deposited hydrogen concentration and tends to follow the as-deposited H concentrations towards larger [O]/([O]+[N]) ratios (see Fig. 11 and Ref. 9). But, if we assume that the concentration of bonding sites for D is given by the initial hydrogen concentration, we are forced to conclude that in N-rich material the H concentration is lower at the surface than in the bulk. The lower values for C_s found for the pre-annealed samples and the 1000 °C treated samples also point in this direction. The uncertainty whether also at 800 and 1000 °C the uptake of D proceeds with a constant C_s precludes a more profound discussion concerning this matter.

We summarize that in the D_2-N_2 anneal treatments we have found a minimum in the values for the total amount of D incorporated, hydrogen removed, and, moreover, in the values for the diffusion coefficients in the [O]/([O]+[N]) range 0.2–0.3. The total amount of D incorporated in the films and the hydrogen diffusion coefficients increase steeply at [O]/([O]+[N]) 0.3. (These increases have also been found in PECVD oxynitrides.[22]) The D incorporation is supposed to proceed via the exchange of gas-phase deuterium with bonded H. Subsequently it diffuses from the surface region deeper into the film. The surface concentrations during the D_2-N_2 anneal are in the range of the initial H concentration and increase with [O]/([O]+[N]) for [O]/([O]+[N])>0.3. The suggestion emerges that the processes of diffusion and exchange are strongly related.

Preannealing at 1000 °C lowers the rate of reaction for all [O]/([O]+[N]) and of $\mathcal{D}$ for the lower [O]/([O]+[N]) values. However, in the LPCVD (and in the PECVD) case the influence of a variation in the oxynitride composition [O]/([O]+[N]) on the reaction and diffusion rates is larger than the influence of preannealing.

V. DESORPTION

A. Desorption of hydrogen from double layers of Si_3N_4

In the preceding sections we discussed the diffusion of D atoms in the bulk of silicon oxynitride films. In this section the subsequent process of D desorption from the surface region of the film is considered. We propose a model in which the desorption occurs through breaking of N-D bonds followed by the escape of D into the inert-gas ambient. It is obvious that this escape can only occur from N-D bonds in the vicinity of the surface. In our (simplified) model we consider the rate of desorption to be nonzero only in a thin surface layer of thickness t_{surf} with a constant D concentration. Furthermore, we assume that the desorption rate is proportional to the N-D concentration in that surface layer. The model leads to the following expression:

$$J_D = \mathcal{K}_{surf} C_{surf} \quad (3)$$

where J_D is the outflux of deuterium atoms through the surface [at./(cm^2 s)], $\mathcal{K}_{surf}$ the reaction rate constant for desorption (cm/s), and C_{surf} the D concentration in the considered surface layer (at./cm^3).

Earlier, when determining the diffusion coefficients (Sec. III), use was made of the shape of diffusion profiles of the HD samples which had been annealed for a limited period, such that the deuterium atoms did not reach the surface and the H+D concentration was not very much decreased.

We now use the *total* D content in the sample in order to derive a value for $\mathcal{K}_{surf}$ for the temperatures 800 and 1000 °C in the case [O]/([O]+[N])=0. A combination of the simulation parameters δ_b and δ_s (see the Appendix) was sought that fits the measured evolution of the total deuterium content in the double-layer structure with time (e.g., Fig. 2). The resulting combination of δ_b and δ_s is not unique. We circumvented this problem by demanding that the combination of δ_b and δ_s must fit the time evolution of the D content of both the HD and the DH structure (see Fig. 2). This analysis yields unambiguous values for the diffusion coefficient $\mathcal{D}$.

The values derived for $\mathcal{K}_{surf}$ amount to $(2.8 \pm 0.5)\times10^{-10}$ cm/s and $(2.3 \pm 0.5)\times10^{-8}$ cm/s for $T = 800$ and 1000 °C, respectively. The corresponding diffusion coefficients obtained in this way amount to 7.5 $\times10^{-14}$ cm^2/s at 1000 °C and 8.4 $\times10^{-16}$ cm^2/s at 800 °C. These values for $\mathcal{D}$ are in close agreement with the earlier obtained values. These results imply an activation energy of 2.6±0.2 eV for both $\mathcal{K}_{surf}$ and $\mathcal{D}$. The value for $\mathcal{D}$ is slightly smaller than the value obtained in Sec. III. This may be ascribed to the fact that treatment of the material at 1000 °C results in a lowering of $\mathcal{D}$. In Sec. III the value for $\mathcal{D}$ at 1000 °C was determined for a very brief period of annealing, during which no significant loss of H+D occurred from the part of the film used for the determination of $\mathcal{D}$. However, in the analysis given here, we also make use of the data after a longer period of annealing and explicitly of the loss of H+D itself. This might result in an underestimation of the 1000 °C value and thus of the obtained activation energy of $\mathcal{D}$. Indeed, the activation energy for $\mathcal{K}_{surf}$ is slightly less but close to the value determined for the activation energy of the diffusion coefficient. We therefore suggest that the same step—breaking of N-H and N-D bonds, respectively—is rate limiting in both the diffusion and the desorption process of hydrogen in SiO_xN_y, in accordance with the desorption model as proposed above.

B. Desorption of hydrogen from thin Si_3N_4 films during annealing

In this section we describe an experimental verification of the first-order dependence of the hydrogen desorp-

tion rate on the hydrogen surface concentration [Eq. (3)]. ND_3 silicon nitride layers as thin as 5 nm have been annealed in inert gas at 650, 700, 800, and 900 °C for periods ranging from 1 min to 3 days. Subsequently, the D content D_{tot} in the film is determined, using ERD. In this case deuterium is applied only for reasons of sensitivity.

For such thin layers we suppose that we can exclude supply of D from deeper layers to the surface layer. We assume the thickness t_l of these layers to be smaller than or about equal to t_{surf} (see Sec. V A). Applying these assumptions to Eq. (3) gives

$$J_D = -\frac{dD_{tot}}{dt} = -\frac{\mathcal{K}_{surf} D_{tot}}{t_l} \quad (4)$$

or

$$D_{tot} = D_0 \exp\left(-\frac{\mathcal{K}_{surf}}{t_l} t\right). \quad (5)$$

In Fig. 13 we plot $\ln(D/D_0)$ versus time, where D_0 is the initial D content. We indeed obtain a linear relationship at 800 and 900 °C. The values for $\mathcal{K}_{surf}$ that are deduced in this manner amount to 4.6 $\times 10^{-10}$ cm/s and 4.6 $\times 10^{-9}$ cm/s for 800 and 900 °C, respectively. These values deviate by a factor of two from those determined in Sec. V A, which is considered to be a reasonable agreement. The resulting activation energy of 2.5 eV agrees very well with the value determined earlier.

We established that the desorption of hydrogen from the Si_3N_4 surface obeys first-order kinetics at 800 and 900 °C with an activation energy close to the =N–H bond energy. We therefore conclude that H desorbs individually from the nitride.

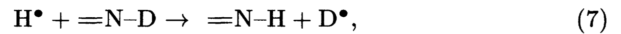
At the lower temperatures, however, deviations from first-order kinetics are observed (Fig. 13). This may have several causes. It is conceivable that at lower T the primary desorption channel is the formation of a H_2 (D_2, H-D) molecule. This process is reported to facilitate H desorption at lower T.[25] Another explanation is that t_{surf} is smaller than the actual layer thickness at $T < 800$ °C, causing a diffusion-limited desorption rate.

VI. MECHANISMS

As we have argumented earlier, the observations are mainly ascribed to the behavior of hydrogen in N-H groups. Therefore, in the discussion of the diffusion process we only consider reactions involving nitrogen bonding sites. We have obtained evidence that the rate-limiting step in the diffusion of hydrogen (or deuterium) is the breaking of =N–H (N-D) bonds:

$$=\text{N–H} \rightarrow\ =\text{N}^\bullet + \text{H}^\bullet. \quad (6)$$

Here $N^\bullet$ and $H^\bullet$ denote (neutral or charged) silicon-bonded nitrogen and unbonded hydrogen. The next step in the diffusion process is transport of the $H^\bullet$ species until it exchanges at a N-D (or N-H) bond site:



$$\text{H}^\bullet +\ =\text{N–D} \rightarrow\ =\text{N–H} + \text{D}^\bullet, \quad (7)$$

or it becomes trapped at a reactive nitrogen site:

$$\text{H}^\bullet +\ =\text{N}^\bullet \rightarrow\ =\text{N–H}. \quad (8)$$

This type of diffusion is described by the Einstein-Smoluchowski equation[27]

$$\mathcal{D} = \frac{\lambda^2}{2\tau}. \quad (9)$$

In this equation $\mathcal{D}$ represents the diffusion coefficient. In our case λ is the mean free path of the emitted $H^\bullet$ species and τ represents the average lifetime of a N-H or N-D bond. The measurement of the surface desorption rate for LPCVD Si_3N_4 (see Sec. V) allows an estimation of the value for τ in the nitride. In an independent measurement we have determined the diffusion coefficients. So, we calculate values for τ of 500 and 50 s at 800 °C

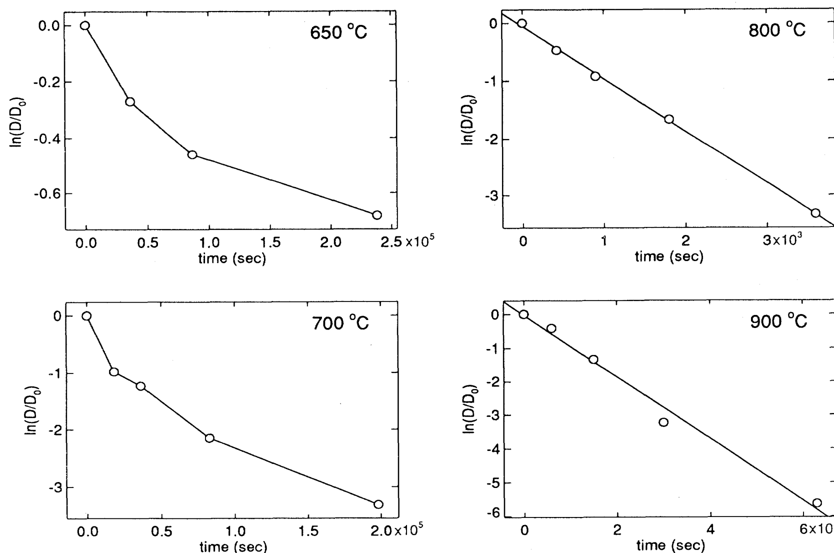


FIG. 13. The D content in 5-nm-thick ND_3 grown Si_3N_4, plotted logarithmically vs time, for various anneal temperatures. A linear fit is shown in the 800 and 900 °C plots.

and 900 °C, respectively. The corresponding mean free paths λ for LPCVD Si_3N_4 amount to 8 and 14 nm. These values are larger than the layer thickness of the nitride used to determine the surface desorption rate. This indicates that the procedure to obtain this quantity is at least internally consistent.

In the model of diffusion as it is presented here, the following parameters are considered to be important: the life time of a =N–H (=N–D) bond (i.e., the inverse of the rate of bond breaking) at the anneal temperature and the mean free path of the unbonded hydrogen radical. The latter quantity in its turn depends on the trapping rate and therefore, among others, on the concentration of trapping and exchange centers. The mean free path of the unbonded $H^\bullet$ is to first order expected to increase with decreasing exchange and trapping site concentration. Since the diffusion process is largely nitrogen related, the nitrogen concentration may be of importance here. However, since a larger concentration of hydrogen than the amount initially present is never incorporated, we suggest that the initial =N–H bond concentration is the relevant parameter. If we assume that the lifetime of a =N–H bond (=N–D) bond is independent of the [O]/([O]+[N]) concentration ratio, then the variation of the diffusion coefficient may be attributed to the variation of the =N–H concentration. Qualitatively, one can conclude that this is indeed the case: the diffusion coefficient is lowest in the [O]/([O]+[N]) region where the H concentration shows a maximum, and the diffusion coefficient increases where there is a decrease in =N–H concentration. However, the decrease of the diffusion coefficient as a result of pre-annealing of the LPCVD nitride films seems to contradict the conclusion given above. Furthermore, the diffusion coefficients in the PECVD material have much higher values than those in the LPCVD oxynitrides, despite of the large =N–H concentrations in PECVD material (see Ref. 22). Also, in the PECVD material a decrease in =N–H content as a result of preannealing at 1000 °C accompanies a decrease in the diffusion coefficient. The inevitable conclusion must be that also material parameters other than the =N–H bond concentration determine the diffusion rate.

It may very well be that the [O]/([O]+[N]) dependence and the thermal history dependence of *both* the diffusion coefficient *and* the =N–H concentration are governed by one and the same parameter. This parameter may be found in the variation of the structure when going from nitride to oxide. Measurement of the [O]/([O]+[N]) dependence of the =N–H bond breaking rate for different temperatures for the various materials and relating this to the diffusion coefficient may be necessary to make one further step in the understanding of these processes.

Although the detailed understanding of the [O]/([O]+[N]) dependence of the diffusion process is not yet complete, the mere observation of the dependence already explains some observations made earlier. A number of electrical and physicochemical properties in the Si-O-N-H thin-film reaction system show a different behavior for [O]/([O]+[N]) values smaller than 0.4–0.5 compared to that above this composition ratio. For instance, the broadening of the hydrogen pile up at the oxide/oxynitride interface during oxidation for the large [O]/([O]+[N]) oxynitrides is probably caused by the larger hydrogen diffusion coefficients in this [O]/([O]+[N]) region.[13,14]

Similarly, the [O]/([O]+[N]) dependence of electrical properties of silicon oxynitride layers can be explained. For instance, the strong decrease in interface state density in LPCVD oxynitride layers with increasing [O]/([O]+[N]) at [O]/([O]+[N])=0.4 (Ref. 12) can now be understood: the larger diffusion rates for the more oxygen-rich oxynitride compositions may result in a more effective interface state passivation by trapping of hydrogen already during the deposition. Furthermore, the appearance of a negative bulk charge for [O]/([O]+[N])>0.4 in the oxynitrides[12,28] can be ascribed to a larger concentration of nitrogen dangling bonds which arise as a result of the faster diffusion of hydrogen at the larger [O]/([O]+[N]) ratios already during deposition. Therefore, it shows that the knowledge of the diffusion phenomena may help to better understand the behavior of (oxy)nitride films in VLSI technology (see also Refs. 29 and 30).

VII. DIFFUSION OF HYDROGEN AND DEUTERIUM THROUGH SiO_2

It has been known for a long time already[31] that hydrogen is able to diffuse at a very high rate through single crystalline silicon. The diffusion coefficient for hydrogen in silicon was reported to be 2×10^{-4} cm^2/s at T=1072 °C with an activation energy of less than 0.5 eV. This raises the question of why hydrogen is not able to escape from the silicon oxynitride through the *c*-Si substrate. One hypothesis is that the native oxide present between the *c*-Si substrate and the deposited oxynitride layer[16] acts as an efficient diffusion barrier.

To investigate a possible effect of an oxide capping on the H desorption a SiO_2 layer of 50 nm thickness was deposited at a temperature of about 600 °C onto the samples DH3, DH5, and DH8 using tetraethylorthosilicate. These layer structures were annealed in Ar at the temperatures 700, 800, 900, and 1000 °C. The as-deposited TEOS layer appeared to contain 3–4 at. % of hydrogen in Si-O-H bonds. This hydrogen disappeared from the TEOS layer already at the lowest anneal temperature of this study (700 °C).

We measured the total amount of D in the layer structure after annealing at various temperatures as a function of the anneal time and compared the data with results of similar experiments on double layers without the TEOS layer. Figure 14 shows a typical result. There is no significant difference in the evolution of the total D contents for the two-layer structures. The 50-nm surface oxide layer apparently offers no barrier for atomic hydrogen to escape into the ambient. We conclude that a thin oxide layer at the oxynitride/*c*-Si interface is unlikely to act as a barrier either.

The fact that we do not observe hydrogen loss through the substrate may be ascribed to the rate of transport

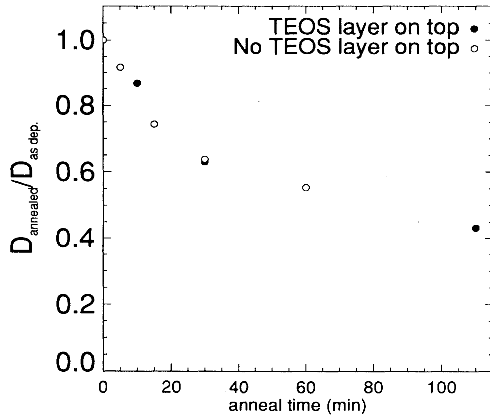


FIG. 14. The deuterium loss vs time for sample HD8, both with and without a silicon oxide layer on top, during annealing at 1000 °C.

through the substrate in comparison to the rate of hydrogen loss through the top surface. The rate of transport through the substrate may be estimated from the known diffusion coefficients and solubility of hydrogen in c-Si. The classic of van Wieringen and Warmoltz[31] contains values for both the $\mathcal{D}$ and the solubility and their temperature dependence. From more recent work on the hydrogen diffusion in c-Si (for a review see Ref. 32) we conclude that the early values of van Wieringen and Warmoltz are correct for p-type substrates. This type of substrate has also been used in this work. If we assume that the H concentration in the substrate is close to the solubility limit (for one atmosphere) at the oxynitride side and zero at the other side of the wafer during annealing in an inert ambient, and take the values of the diffusion coefficient of Ref. 31, the flux of hydrogen through a wafer of 0.5 mm thickness amounts to 1×10^{12} at./(cm^2 s). This quantity is much lower than the amount desorbing at the surface at 1000 °C in our experiments [about 5×10^{13} at/(cm^2 s)]. Therefore, the H loss through the c-Si substrate is—under the conditions used in this study—estimated to be of the order of a few percent of the loss into the ambient. In general, the rate of H transport through the substrate will depend on wafer type and thickness, temperature, and oxynitride thickness.

VIII. CONCLUSIONS

Our investigations of the concentration profiles of hydrogen and deuterium in layers of LPCVD silicon nitride and oxynitride films has led to the following conclusions.

(i) Release of hydrogen from silicon oxynitride proceeds through the diffusion of (mainly nitrogen) bonded hydrogen to the surface and subsequent desorption from a surface layer of several nanometers thickness.

(ii) The diffusion coefficient of hydrogen (or deuterium) is in the range between 3×10^{-18} and 1×10^{-13} cm^2/s, at temperatures between 700 and 1000 °C, and is characterized by a single activation energy of 3 eV, for [O]/([O]+[N]) values up to 0.45. This value identifies the =N–H bond breaking as the rate-limiting step in the diffusion process. The diffusion coefficient has a minimum for [O]/([O]+[N]) in the range 0.2–0.3. We have found a strong increase of the diffusion coefficient for [O]/([O]+[N])>0.3.

(iii) The diffusion coefficients determined in double layers, deposited from ND_3 (and NH_3), and those determined from experiments with the oxynitrides annealed in a D_2-N_2 ambient are equal. This indicates that in either case the diffusing species is equal.

(iv) The process of D uptake is identified as an exchange process between H bonded in the film and D supplied from the gas phase. The indiffusion can be described consistently by assuming a surface layer with constant D concentration from which the D diffuses deeper into the film (at 900 °C).

(v) Preannealing of the silicon oxynitride layers at 1000 °C results in a decrease of the exchange and diffusion rates, notably at [O]/([O]+[N]) ratios below 0.3. This is explained by the decrease of the concentration of available hydrogen (or deuterium) bonding sites during the high-temperature pretreatment. Thus this concentration has been identified as a relevant parameter in the diffusion and exchange process. This effect also explains the relative decrease in the relevant rates when the as-deposited samples are annealed at a temperature of 1000 °C. In this respect, the oxynitrides can be considered stable at 900 °C, but not at 1000 °C on a time scale of a few minutes.

(vi) Although we have been able to reveal many details of the dynamic behavior of hydrogen in (oxy)nitrides, the origin of the [O]/([O]+[N]) dependence of $\mathcal{D}$ and the desorption and exchange rates are still unclear. However, the similarity of the [O]/([O]+[N]) dependence of the processes of diffusion, exchange with the gas phase, and desorption in inert-gas ambient indicates that the rate-limiting steps are very much related.

APPENDIX: DIFFUSION COEFFICIENT

In this appendix we describe the method we used to determine the diffusion coefficients in the various samples by comparing the ERD deuterium-concentration depth profiles with profiles obtained using a computer program[33] that simulates a diffusion process according to Fick's diffusion equation. See Secs. III and V A for some notational conventions. In one dimension

$$\frac{\partial C}{\partial t} = \mathcal{D}\frac{\partial^2 C}{\partial x^2}, \tag{A1}$$

where $\mathcal{D}$ is the diffusion coefficient, C the concentration, t the time, and x the depth. Conceptually, the sample is divided into n slabs of thickness Δx each. The shape of the concentration depth profile of the considered species is evaluated repeatedly using the discrete version of Eq. A1. For slabs $2, \ldots, n-1$ we have

$$C_{i,j+1} = C_{ij} + \frac{\delta_b}{(\Delta x)^2}\left(C_{i-1,j} + C_{i+1,j} - 2C_{ij}\right), \tag{A2}$$

where C_{ij} is the concentration in slab i after step j and δ_b is a constant, chosen such that $Drb \ll (\Delta x)^2$.

The flow into and out of the layer at the surface is determined by δ_s. For the first slab

$$C_{1,j+1} = C_{1j} + \frac{\delta_b}{(\Delta x)^2}(C_{2j} - C_{1j}) + \frac{\delta_s}{\Delta x}(C_g - C_{1j}), \tag{A3}$$

where C_g is the concentration in the gas outside the layer. The flux at the interface with the substrate is negligible in this experiment. The initial values C_{i0} are determined by the details of the deposition process only. The goal of the procedure is to find, for each deuterium profile, parameters δ_s and j for which the best fit of the calculated profile with respect to the data is obtained. The calculated deuterium profiles we convoluted with the depth-dependent depth-resolution function in order to allow for a proper comparison with the measured ERD profiles. We used χ^2 as a goodness of fit. The diffusion coefficient $\mathcal{D}$ is calculated from δ_b and j:

$$\mathcal{D} = \frac{\delta_b j}{t}, \tag{A4}$$

where t is the actual annealing time. The reaction-rate constant for desorption $\mathcal{K}_{\rm surf}$ is obtained from δ_s using

$$\mathcal{K}_{\rm surf} = \frac{\delta_s j}{t}. \tag{A5}$$

---

*Present address: Technical University Eindhoven, P.O. 513, 5600 MB Eindhoven, The Netherlands.

[1] R. A. Street, J. Kakalios, C. C. Tsai, and T. M. Hayes, Phys. Rev. B **35**, 1316 (1987).

[2] S. C. Li and S. P. Murarka, J. Appl. Phys. **72**, 4214 (1992).

[3] P. V. Santos and W. B. Jackson, Phys. Rev. B **46**, 4595 (1992).

[4] F. H. P. M. Habraken and A. E. T. Kuiper, Thin Solid Films **193**, 665 (1990).

[5] H. J. Schliwinski *et al.*, J. Electrochem. Soc. **139**, 1730 (1992).

[6] V. J. Kapoor, D. Xu, R. S. Bailey, and R. A. Turi, J. Electrochem. Soc. **139**, 915 (1992).

[7] H. J. Stein and H. A. R. Wegener, J. Electrochem. Soc. **124**, 909 (1977).

[8] H. J. Stein, P. S. Peercy, and R. J. Sokel, Thin Solid Films **101**, 291 (1983).

[9] F. H. P. M. Habraken *et al.*, J. Appl. Phys. **59**, 447 (1986).

[10] J. A. Topich and R. A. Turi, Appl. Phys. Lett. **41**, 641 (1982).

[11] J. Remmerie *et al.*, in *Silicon Nitride Thin Insulating Films,* edited by V. J. Kapoor and K. T. Hankins (The Electrochemical Society, Pennington, NJ, 1987), Vols. 87–10, p. 50.

[12] M. Heyns *et al.*, in *LPCVD Silicon Nitride and Oxide Films, Material and Applications*, edited by F. H. P. M. Habraken (Springer, Heidelberg, 1991), Chap. 4, p. 82.

[13] A. E. T. Kuiper *et al.*, J. Vac. Sci. Technol. B **7**, 455 (1989).

[14] J. B. Oude Elferink, Ph.D. thesis, Utrecht University, the Netherlands, 1989.

[15] W. M. Arnoldbik and F. H. P. M. Habraken, Rep. Prog. Phys. **56**, 859 (1993).

[16] A. E. T. Kuiper, S. W. Koo, F. H. P. M. Habraken, and Y. Tamminga, J. Vac. Sci. Technol. B **1**, 62 (1983).

[17] W. M. Arnoldbik *et al.*, Appl. Phys. Lett. **56**, 2530 (1990).

[18] J. B. Oude Elferink *et al.*, Appl. Surf. Sci. **30**, 197 (1987).

[19] P. S. Peercy, H. J. Stein, B. L. Doyle, and V. A. Wells, in *Proceedings on the Seventh International Conference on Chemical Vapour Deposition, Los Angeles*, edited by T. O. Sedgwick and H. Lydtin (Electrochemical Society, Pennington, NJ, 1979), Vols. 97–93, p. 198.

[20] G. Schols and H. E. Maes, in *Silicon Nitride Thin Insulating Films*, edited by V. J. Kapoor and H. J. Stein (The Electrochemical Society, Pennington, NJ, 1983), Vols. 83–88, p. 94.

[21] S. M. Repinsky, in *Silicon Nitride in Electronics*, edited by V. I. Belyi *et al.* (Elsevier Science, Amsterdam, 1988), Vol. 34, p. 99.

[22] W. M. Arnoldbik, C. H. M. Marée, and F. H. P. M. Habraken (unpublished).

[23] W. M. Arnoldbik, Ph.D. thesis, Utrecht University, the Netherlands, 1992.

[24] J. Crank, *Mathematics of Diffusion*, 2nd ed. (Oxford University Press, Oxford, 1975).

[25] C. M. M. Denisse *et al.*, J. Appl. Phys. **60**, 2543 (1986).

[26] F. H. P. M. Habraken *et al.*, in *LPCVD Silicon Nitride and Silicon Oxynitride Films*, edited by F. H. P. M. Habraken, (Springer, Heidelberg, 1991), Chap. 1.

[27] P. W. Atkins, *Physical Chemistry*, 4th ed. (Oxford University Press, Oxford, 1990).

[28] F. H. P. M. Habraken *et al.*, in *LPCVD Silicon Nitride and Oxide Films, Material and Applications* (Ref. 12), Chap. 5, p. 118.

[29] J. Robertson, Appl. Phys. Lett. **59**, 3425 (1991).

[30] Y. Roizin, J. Non-Cryst. Solids **137**, 61 (1991).

[31] A. van Wieringen and N. Warmoltz, Physica **22**, 849 (1956).

[32] S. J. Pearton, J. W. Corbett, and J. T. Borenstein, Physica B **170**, 85 (1990).

[33] M. J. van den Boogaard, Ph.D. thesis, Utrecht University, the Netherlands, 1992.